A TEXT BOOK OF CHEMISTRY

VOL I

B.C. SEN

FOR
HIGHER SECONDARY
STUDENTS

A Mukherjee & Co Pvt Ltd

A TEXT BOOK OF CHEMISTRY

[VOLUME I]

PART I—General Principles
PART II—Non-Metals

Written according to the New Syllabus introduced by the West Bengal Council of Higher Secondary Education for Classes XI & XII

A TEXT BOOK OF CHEMISTRY

Volume I

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PREFACE

This is a comprehensive Text Book in Chemistry and designed primarilly to meet the requirement of students at the plus two level of the (10+2+3) pattern of education. It covers the new syllabi of the West Bengal Council of Higher Secondary Education and the All India Higher Secondary Course. This is the First Volume of the Text Book which includes all the topics meant for Paper I and are usually taken up in Class XI. The Second Volume will come out in due course.

In the new system of education, the Higher Secondary level is very important and crucial as it forms the bridge between the elementary course taught in Secondary Schools and the advance course followed in Colleges and Universities. If the students are not well acquainted with this course, it will be difficult for them to proceed with the advance studies in Chemistry. This introductory text book has been written in a most lucid and comprehensive way without sacrificing accuracy in order to provide an easy understanding of the principles of Chemistry with a fairly wide range of their applicability to the students of +2 level. The logical development of the subject will create interest in them. The book is also provided with the most up-to-date methods of production of substances with a large number of sketches and diagrams. Sufficient number of problems have been worked out and many more are given as exercises. At the end of each chapter several well graded as well as objective type questions are included which will be very helpful for the students to stimulate their independent thinking. The book will also help them in their preparation for admission to the Engineering and Medical Institutions.

I must express my sincere thanks and gratitude to Dr P. C. Rakshit, formerly Head of the Department of Chemistry, Presidency College, Calcutta for his valuable suggestions and guidance, which helped me in writing this book. I also acknowledge the Co-operation received from M/s. A. Mukherjee and Co., Calcutta for Publishing the book on Schedule. Any comments and valuable suggestions for the improvement of the book from the readers will be much appreciated.

Calcutta
30.6.86

B. C. SEN.

SYLLABUS

CHEMISTRY

Full Marks—200

PAPER—I (Marks—70)

GROUP—A

General and Physical Chemistry (Marks—40)

I. Laws of Chemical Combination—Dalton's Atomic Theory (critical study), Gay Lussac's Law. Atomic Weight.

II. Concept of the molecule and Avogadro's hypothesis. Definition of molecular weight. Simple deductions from Avogadro's hypothesis, Elementary idea about Avogadro's Number. Mole concept—numerical problems on the concept.

III. Chemical Equation—different types and their significance. Stoichiometry—weight to weight, weight to volume and volume to volume calculations. Eudiometry and problems on Eudiometry. Vapour density, empirical fromulae and molecular formulae.

IV. Equivalent weights. Determination of equivalent, atomic and molecular weights (Mol. wt by victor Mayer's method only). Dulong and Petit's law. Mitscherlich's law of isomorphism—numerical problems.

V. Acids, bases and salts. Arrhenius concept of and bases. Different types of oxides, oxyacids, hydroxides and hydracids. Hydrolysis of salts. Equivalent weight of acids, bases and salts. Standrad solutions: normal (and formal) and molar solutions. Neutralisation, acid-base indicator. Chemical calculations on acidimetry and alkalimetry.

VI. Boyle's law, Charle's law, Gas Constant R ; $PV = nRT$. Dalton's law of partial pressure, Graham's law of diffusion of gases. Numerical problems.

VII. Solution of solid in liquid. Solubility. Saturated, unsaturated and supersaturated solutions.

Solubility curves and determination of solubility.

Crystallisation, fractional crystallisation, water of crystallisation and its determination. Colloids and dialysis.

VII. Conducting and non-conducting solutions—Arrhenius. theory.

Electrolysis—Faraday's laws of Electrolysis.

Electrochemical equivalent $\frac{F}{N} = e$

IX. Law of Mass Action. Dynamic equilibrium and equilibrium constant. Le Chatelier's principle and its application with special reference to ammonia, nitric acid, sulphuric acid.

(Note : Numerical problems on Law of Mass Action are not required).

GROUP—B

Inorganic Chemistry (Marks : 30)

The Chemistry of an element or a compound mentioned in this syllabus includes preparation, properties, reactions and uses.

I. Oxygen and hydrogen, water, hard and soft water. Softening of water : boiling, lime soda process and ion-exchange method. Hydrogen peroxide and ozone.

II. Air, Nitrogen, NH_3 N_2O, NO, N_2O_4, HNO_2, HNO_3.

III. Boron (from B_2O_3 by Mg reduction), Orthoboric acid, Borax.

IV. Carbon, CO, CO_2, Carbonic acid.

V. Phosphorus, PH_3, P_4O_6, P_4O_{10}, H_3PO_3, H_3PO_4.

VI. Sulphur, H_2S, SO_2 SO_3, H_2SO_3, H_2SO_4.

VII. Halogens : Fluorine, Chlorine. Bromine and Iodine—a comparative study ; Hydracids.

VIII. Large scale preparation (omitting details) with reference to the physico-chemical principles involved, wherever applicable, of the following :

Hydrogen, Ammonia, Nitric acid, Sulphuric acid (contact process only). Coal-gas.

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PART I

(GENERAL PRINCIPLES)

CHAPTER I

INTRODUCTION

1.1. **Introduction** :— Everyday we come across with large number of substances around us which are perceived by one or more of our senses. These substances are characterised by distinct properties which differentiate one object from another. They undergo various changes either spontaneously or by the application of external forces. For example, a piece of iron rusts when kept exposed to moist air, Coal burns to give both heat and light with the formation of ash, hard rocks are converted to soils by the action of wind, rain etc. By observing such events in the universe and by collecting results of specially contrived experiments performed in the laboratory, facts are accumulated. Man, as an inquisitive and speculative being, attempts to systematise all these facts by bringing Co-ordination and Correlation among them. This Co-ordinated systematised pattern of knowledge is Science.

The aim of science is to devise a structure of the material Universe which will explain all that goes on in it, and predict their future behaviour. This is done by formulating laws and framing theories and hypothesis for their explanation. From observations and experiments facts accumulate. These facts are arranged and classified as far as possible in a rational manner. When observations and experiments of the same kind yield similar results, it becomes possible to combine these results in a single statement or law. Hence a *law* may be defined as the summarising statement of a large number of experiments or observations of the same kind. When a series of laws are established, attempts are made to explain these laws by constructing a mental picture called *hypothesis*. This has contributed much towards the development of Science. It requires the imagination of some structure or mechanism of the simplest possible character, having properties which would enable it to behave in conformity with the laws. A hypothesis must not only embrace several laws and account for all known facts, but also predict some experimental result which had not been previously expected. But when experiments fail to confirm its predictions, the hypothesis is either to be rejected or modified. When a hypothesis survives these tests and is found to be in harmony with all the known facts in a given field, it becomes a *theory*. A theory may be modified with new discoveries. By the process of deducing laws and devising hypotheses and theories to account for them, Science endeavours to provide a model of the working of the universe in terms of which all events can be explained. Scientific discoveries are often the result of such endeavours.

With the gradual accumulation of very large number of facts from generation to generation, Science divides and subdivides itself into intermerging branches for the convenience of study and investigation. In this fashion grew up the various branch of Science, such as, Mathematics, Physics, Chemistry, Botany, Zoology, Physiology, Astronomy, Geology, Geography and so on. Of these chemistry is concerned with matter and its changes.

Chemistry :—Chemistry is one of the oldest branches of natural science. Undoubtedly, it had its origin in technical arts and crafts of primitive civilization when human minds tried to create new things for easier and better life. Then through ages this branch of Science had developed enormously due to various discoveries and inventions. Chemistry really deals with the study of matter, its properties, composition, uses and the changes it undergoes in different conditions. It is concerned not only with the transformation of matter but also with the energy changes accompanying such transformation.

The scope of chemistry is so extremely wide and accumulated knowledge is so vast that it has been found necessary to divide the subject into several sections so that it may be studied more thoroughly and with proper justice. The chief divisions are (a) Physical Chemistry, (b) Inorganic Chemistry and (c) Organic Chemistry.

Physical Chemistry deals with the Scientific laws and principles that govern transformations of matter. It is really a borderline subject, where various chemical phenomena have been explained and predicted with the help of lofty imaginations of physics and the logical application of mathematical reasonings.

Inorganic Chemistry is mainly concerned with the study of mineral matter and deals with the study of elements and their compounds (except carbon and its componnds).

Organic Chemistry is the chemistry of carbon compounds. The element carbon has been found to produce a very large number of compounds which are important in the fields of life processes. This branch of chemistry mainly deals with the products of plant and animal origin, viz, proteins, fats and oils, carbohydrates, vitamins, dyes, drugs etc.

Besides these three main divisions, chemistry is also studied under several other branches like, Biochemistry, Applied chemistry, Analytical chemistry, Nuclear chemistry, Soil chemistry etc.

1.2. **Chemistry as an experimental Science** :—As already said, Chemistry deals mainly with the study of the properties of matter and their transformations. For such study it is essential to collect facts either by observing natural events that take place in the Universe or by performing experiments in the laboratories. Such experiments produce many important results which are collected, analysed and definite inferences are drawn about the particular process. We feel the existence of air easily when wind blows. But that air is a mixture of several gases, its density changes with the variation of temperature and pressure and other such informations cannot be obtained unless we perform various experiments with air. Hence in the study of chemistry, always experiments are done in the laboratories and observing the results of such experiments, important inferences are drawn.

Philosophical speculations are not of any importance. Hypothesis or theory which cannot survive the experimental tests, has to be modified in such a way so that the new theory can explain the observed experimental facts. Thus the study of chemistry depends largely on experimental results, it is treated as an experimental science.

The science of chemistry has not only helped us to acquire the systematic and coordinated knowledge about all sorts of chemical process in this universe and constitutes a considerable part of our rudimentary knowledge of nature, its knowledge has helped to discover many valuable and useful substances which are beneficial to the entire mankind. Dyestuffs, medicines and drugs, food preparations, soaps and other detergents, fertilizers and insecticides, synthetic rubber and petrol, explosives, metals and alloys, artificial fabrics, acids and alkalies, plastics, paints and varnishes are some of the essential and, indeed, indispensable products of the modern chemical industry.

1.3. History of the developement of Chemistry :—

As already stated, the science of chemistry had its origin in technical arts and crafts of primitive civilisation. Then through ages this Science had developed into the present day modern chemistry. The civilisation of ancient Egpypt, India, China, Sumer, Greek all made positive contribution's to its development. Of all the early civilised people, the Egyptians were really a practical race and developed the art of chemistry greatly. The Greek and Indian philosophers made speculations about the physical background of the universe and the units of composition of matter. Apart from the metaphysical speculations of these ancient civilisation, there are three distinct stages in the development of science of chemistry, they are the periods of (i) Alchemy upto the fifteenth century—during this period the chief aim was to find out philosophers stone and universal solvent for transmutation of base metals into gold. (ii) Iatro Chemistry from the 16th century upto the middle of the 17th century—when attempts were made to discover elixir of life which would cure all diseases and (iii) Scientific Chemistry—when the study of chemistry was taken up for its own sake, the era of scientific chemistry began with Robert Boyle (1627–91).

Some important stages with age in the development of chemistry have been shown in the following chart. *

A. D. 1900		
	Modern Chemistry established and developed.	
1800	Priestley discovered oxygen ; Cavendish, Scheele, Lavoisier.	
	Boyle—the Founder of Modern Chemistry.	
1600	Van Helmont—Medical or Iatro Chemistry. Search for "Elixir of Life".	
	Paracelsus	Period of Alchemy. Transmutation of Base Metals into Gold Philosopher's Stone.
1400	Basil Valentine	
1200	Roger Bacon discovered Gunpowder.	
1000		
800	Geber wrote Treatise on Alchemy. Muslim Empire extended to Spain. Spread of Alchemy.	
600	Arabs conquered Egypt ; wrote books on subject of Alchemy.	
400		
200	First Books on chemeia (The Divine Art) written by Greeks in Alexandria.	
	Brass (alloy of copper and Zinc) used in Roman Coinage.	
1000 B.C.		
2000 B.C.	Pottery, Glass, Vegetable Dyes, Medicines (Egypt)	
3000 B.C.	Alloys first made e.g., Bronze (Egypt)	
3500 B.C.	Metals : Gold, Copper, Silver, Lead, Tin were isolated from their minerals and used (Egypt).	

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* Taken from "New Educational Library" ; Physical Science.

1.4. Matter : Chemistry deals with the study of material objects and the transformation they undergo. What is matter or a material object ? Any substance which has its existence and of which the universe is built and is perceived by one or more of our senses is called matter. For example water, air, stone, tree, iron, salt, sugar, table etc. are all considered as matter. These material objects differ in shape, size, colour and other properties. Sugar, a white substance is sweet in taste, glass is brittle and transparent, gold is a solid possessing golden-yellow colour and lusture. These differences in essential properties are due to the fact that substances differ in composition. Though the differnt kinds of materials differ in properties and composition, they possess some common features. All of them occupy some space, possess some mass (hence weight), and requires certain amount of force to alter their state of rest or of motion (inertia). *Matter, therefore, may be defined as anything that is perceived by our senses, and which possesses mass (and hence weight), occupies space and changes position only on application of external force.*

Three states of matter : Various kinds of matter that are found on earth may exist in any one of the three states of aggregation at a given temperature and pressure, viz, solid, liquid and gaseous. **A solid** has a definite shape and volume mainly due to its rigidity. Both the volume and the shape can only be altered by the application of considerable force. Salt, Ice, Sand, Chalk, Iron, Coal etc are all solids. **A liquid** has a definite volume but no definite shape. Due to its fluidity it takes the shape of the vessel in which it is placed. Liquids are compressible under pressure and expand with increase of temperature, but such changes are extremely small. Water, oil, glycerine, alcohol, benzene, mercury etc. are some of the examples of liquid substances. **A gas** has neither, any definite shape nor any definite volume. If a gas is introduced in an empty vessel, it fills the vessel uniformly and completely. The gaseous state of matter is also characterised by low density, high compressibility and thermal expansibility. Air, oxygen, nitrogen, carbondioxide are examples of gaseous substances. Liquids and gases are both termed as fluids.

Every matter is composed of very minute particles. These particles, we shall see later, are called molecules. The difference among three states of matter is that—

(i) in **solids**, the molecules are in close proximity and as such the intermolecular forces are very high. The molecules cling to one another and they have no translational motion. In consequence, the solids have definite shape and volume.

(ii) in **liquids**, the molecules have less intermolecular force and as such these can move some what freely. The intermolecular space is larger. As a result the liquids have definite volume but they change their shape with that of the container. (iii) in **gases**, the molecules have least intermolecular force and these fly away from one another. The intermoleculer space is large. Due to lack of rigidity they have neither a given shape nor volume.

The same substance may exist in all the three states depending upon the temperature and pressure. A substance may pass from one state to another by the application or withdrawal of heat. Thus ice (solid) melts and is converted into liquid (water) when it is heated and water is transformed into steam (gaseous) when it is farther heated. Similarly, on cooling the reverse process takes place. Substances like iron, lead, mercury, paraffin wax etc. also behave in the similar way.

$$\text{Solid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{liquid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{gas}$$

A solid in the pure state will melt at a definite temperature under normal atmospheric pressure. This temperature is called the melting point of the solid and the process of converting a solid into a liquid state by heating is called fusion. In the reverse process the liquid will freeze at the same temperature when cooled. This temperature is called the freezing point of the liquid. For a pure substance, the melting point and the freezing point must be the same. Thus ice melts at 0°Ca nd water freezes also at 0°C under one atmospheric pressure. The melting point of lead is 327°C.

Similarly, when a pure liquid substance is heated its temperature rises and begins to boil at a fixed temperature under normal atmospheric pressure. This temperature is called the boiling point of the liquid and the process of converting a liquid into the vapour state is called vaporisation. Water boils at 100°C under one atmospheric pressure. The boiling point of mercury is 357°C. The reverse process of converting a vapour into the liquid state by cooling is called condensation.

There are, however, some substance, which are converted from the solid state directly into the vapour state on heating under normal atmospheric pressure without passing through the liquid phase. This phenomenon is called sublimation. Examples are iodine, ammonium chloride etc.

It may, however be mentioned that a substance may exist in more than one state at equilibrium under certain conditions of temperature and pressure. Thus, water, ice and water vapour can co-exist at 0·01°C and at a pressure of 4·57 mm. of Hg. This is called the tripple point of water.

1.5. **Classification of Matter :** Different kinds of matter or substances may be classified broadly into two classes—(1) *homogeneous* and (2) *heterogenous*.

In a homogeneous substance, the composition and properties remain the same throughout the whole mass of the substance. It consists of one type of substance only. Hence all pure substances which contain only one kind of matter are homogeneous. Water, salt, sugar, iron, mercury, alcohol, carbondioxide etc. are all homogeneous substances. Some mixtures, however, though not pure, are homogeneous. When some sugar or salt are dissolved in water, such solutions form perfectly homogeneous mixtures. Similarly, different gases can mix together to form homogeneous substance. Thus air is a homogeneous mixture of nitrogen and oxygen mainly.

A heterogeneous substance is a mixture of two or more materials and show different composition and properties in its different parts. The different parts of a heterogeneous substance, which are physically distinct and mechanically separable, are called phases. Gunpowder is a heterogeneous substance, which is a mixture of charcoal, sulphur and nitre. Milk, blood, soil, muddy water, paints and varnishes—are all examples of heterogeneous substances.

Pure homogeneous substances are again classified into two types—(i) *elements* and (ii) *compounds*, according to their composition. Some chemical substances such as iron, copper or gold, when heated, cooled, subjected to the action of an electric current, or treated with acids alkalis or other chemicals, will either remain unaffected or they will produce new chemical substances of which they form only part. The original substances will not be broken down into any simpler substances with different properties. Such chemical substances are known as elements. Iron is an element as it cannot be decomposed into anything simpler than iron. *Hence, elements are defined as homogeneous substances which cannot be decomposed into any simpler substances of different characteristics by any physical or chemical means.* Iron copper, silver, gold, sulphur, carbon, lead, mercury, oxygen, hydrogen etc. are few familiar elements.

There are other chemical substances which may be broken down into two or more simpler substances, i.e. the elements, by chemical or physical methods. These are known as *compounds.* Water is a compound as it can be decomposed into two gaseous elements, hydrogen and oxygen, by passing electric current through it. Chalk or calcium carbonate when heated yields carbondioxide and calcium oxide, which on further treatment produce carbon, oxygen and calcium. Hence, *Compounds are defined as homogeneous substances which are formed through chemical combination of two or more elements in definite proportion by weight and hence, they can be decomposed into two or more different substances by chemical or physical methods.* Water, Salt, Sugar, Copper sulphate, Washing soda, Sulphuric acid, lime—are all well-known compounds.

Most of the chemical substances, which exist in nature or prepared in the laboratory, are compounds. In comparison the number of chemical elements are few. There are about 105 elements known, some of which (like Neptunium, Plutonium etc) are prepared artifically in the laboratory.

N. B. Although no element can yield any other element by ordinary methods, but the discovery of radioactivity and the preparation of elements by artificial methods have changed this idea. During radioactive disintegration, Radium, a radio-active element, is produced from Uranium, another radio-active element. Hence it is necessary to change the definition of elements slightly. This will be discussed in subsequent chapter.

Some of these elements are found in nature in the free state, e.g. Gold, Sulphur, oxygen, nitrogen etc. But most of them are found in combination with other elements producing thousands and thousands of different compounds of which the universe is built. About 98% of the earth's crust including the ocean and the atmosphere are made up of eight most common elements. These are oxygen, silicon, aluminium, iron, calcium, sodium, potassium and magnesium,—representing the decreasing order in their relative abundance. Oxygen alone constitute about fifty percent of the earth's crust. The distribution of elements in the earth's crust is shown in the following diagram. (fig. 1-1)

Metals and Non-metals : —The elements have been further divided into two main classes, metals and non-metals, depending upon their characteristic properties. Such a division, though useful, is somewhat arbitrary, since some elements possess properties of both metals as well as non metals. They are called metalloids—the elements arsenic, antimony etc. belong to this category.

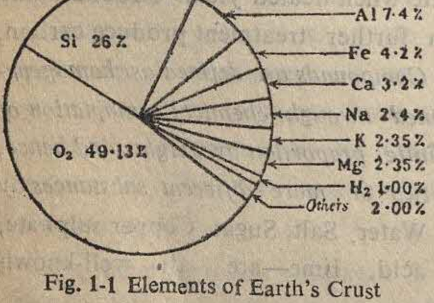


Fig. 1-1 Elements of Earth's Crust

The metallic elements or metals like iron, nickel, copper, lead, silver, gold, zinc, magnesium, aluminium, potassium, etc. always possess certain distinctive properties. They are generally solids (except mercury which is liquid), good conductors of heat and electricity, possess lusture and emit sound when struck. Metals also possess tenacity and toughness. malleability and ductility i.e. they can be hammered into thin sheets and drawn into wires.

On the other hand, the non-metals like Oxygen, Nitrogen, Chlorine, Bromine, Iodine, Sulphur, Phosphorus etc. are generally gases or volatile solids or liquids. They are poor conductor of heat and electricity (except graphite which is good conductor) and possess no metalic lusture (except graphite and iodine, both have some lusture). The non-metals are not malleable or ductile—they are brittle, if solid.

In chemical properties also metals differ from non-metals—this will be discussed later.

Mixture or Mechanical mixture : Substances also occur as mixtures which are generally heterogeneous in character. A mixture is obtained when two or more different substances (elements or compounds) are simply mixed together in any proportions without undergoing any chemical union. Hence in a mechanical mixture the component substances remain side by side, retaining their individual properties and are separable by easy methods, like decantation, filtration, distillation, sublimation etc.

The gun-powder is a mixture of three substances, charcoal, sulphur and nitre. Air is mainly a homogeneous mixture of gases like nitrogen and oxygen.

1.6. **Mixture and Compounds** :—Both the mechanical mixture and the chemical compound are composed of two or more different substances. But in the former case, the components are merely blended retaining their own properties, whereas in the latter case, they have combined chemically loosing their individual properties and entirely a new substance is formed. Hence a mixture differs from a compound. The following illustration will clearly show the distinction between them.

Some amount of iron filings and powdered sulphur are mixed thoroughly to form a mechanical mixture.

(1) By means of a lens, it can be seen that both iron and sulphur remain side by side in the mixture thus prepared.

(2) The iron filings can be removed from the mixture if a magnet is brought near it as iron is attracted by the magnet. Sulphur will be left behind. Similarly, if a small amount of the mixture is added to dilute hydrochloric acid in a test tube, hydrogen gas is evolved by the reaction of iron with hydrochloric acid. Sulphur remains unaffected.

(3) If liquid Carbon-di-Sulphide is added to a small amount of the above mixture in a test tube and is shaken well, Sulphur will go into solution leaving behind iron. After filtration, sulphur is obtained from the solution by evaporation of Carbondi-Sulphide.

Hence it is clear that both the Components of the mixture, Iron and sulphur, retain their own properties. No new substance is formed by such mixing.

Now a mixture of 7 gms of fine iron filings and 4 grms of powdered Sulphur are mixed thoroughly and is heated in a test tube. The whole mass will glow with the evolution of much heat. On cooling, a black mass is obtained which is powdred in a mortar after breaking the test tube.

(1) By means of a lens neither iron nor sulphur can be identified.

(2) Magnet cannot now separate iron from sulphur as the iron lost its separate existance. Also no hydrogen gas is evolved when this powder is added to dilute hydrochloric acid.

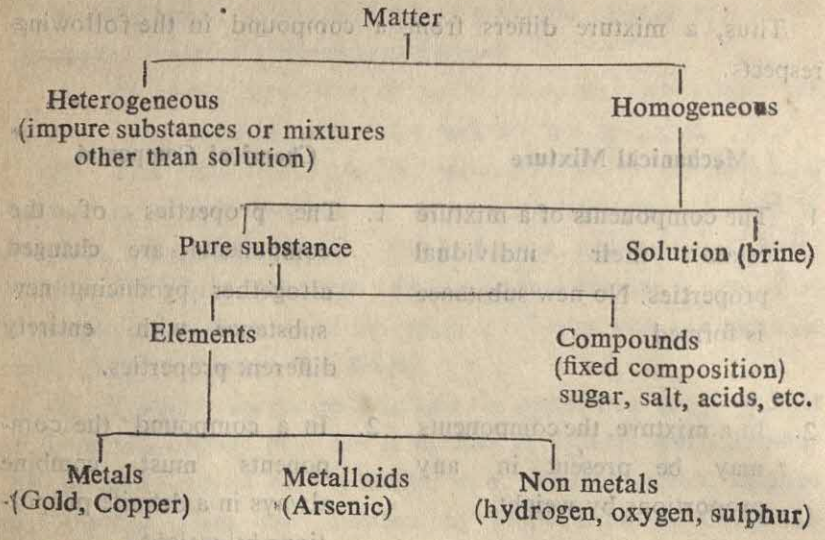
(3) If liquid Carbon-di-sulphide is now added to a small amount of this powder in a test tube, Sulphur will not go into solution as it looses its separate existance.

Hence it is clear that by the application of heat to the mixture of iron and sulpher in a fixed proportion, a chemical reaction takes place resulting entirely a new compound, loosing their individual properties.

Thus, a mixture differs from a compound in the following respects.

Mechanical Mixture	Chemical Compound
1. The components of a mixture retain their individual properties. No new substance is formed.	1. The properties of the components are changed altogether producing new substance with entirely different properties.
2. In a mixture, the components may be present in any proportions by weight.	2. In a compound, the components must combine always in a definite proportions by weight.
3. The components of a mixture may be separated by easy physical methods like filtration, distillation, sublimation etc.	3. The components of a compound can not be separated easily by simple physical methods.
4. Thermal change may or may not occur during the formation of a mechanical mixture.	4. Heat will be evolved or absorbed whenever a chemical compound is formed.
5. A mixture may be homogeneous but usually is heterogeneous.	5. A compound is always homogeneous.
6. A mixture has no fixed melting or boiling points.	6. A compound, being a pure substance, has fixed melting and boiling points.

Various classifications of matter may be summerised as follows :—



1.7. Separation of Components of a mixture :

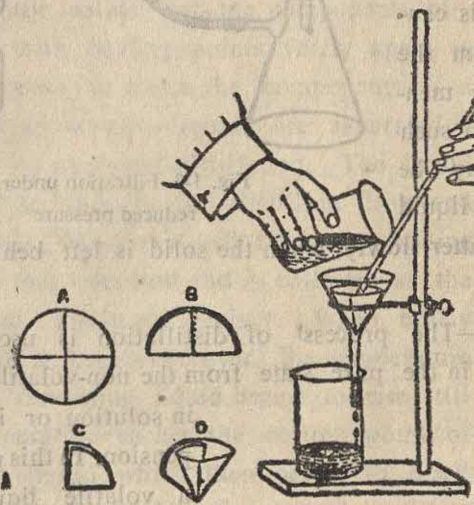
It has been mentioned that the components of a mixture can be separated easily by some common laboratory processes such as decantation, filtration, distillation, sublimation etc. These simple laboratory processes are described below.

(1) **Sedimentation and Decantation** :—By this process an insoluble heavy solid can be separated from a liquid. If a small amount of muddy water is taken in a beaker and is allowed to stand undisturbed for some time, the clay particles, being heavier, will gradually settle down at the bottom, leaving a clear water at the top. This process of settling is known as sedimentation and the settled solid is known as the sediment.

After settling, the clear supernatant liquid at the top may be carefully poured off without disturbing the sediment. This process is known as decantation.

(2) **Filtration** :—By this process an insoluble solid, both heavier and lighter than a liquid, can be separated from the liquid more efficiently and completely by allowing the mixture to pass

through a porous material. such as filter paper, which allows only the liquid to pass through, but not the solid. In the laboratory, filtration is done with the help of circular filter paper, which is folded into quarters and then opened out with three folds on one side and one on the other so that a cone is formed. (Fig 1.2) It is then fitted in a glass funnel which is kept on a stand. The mixture of liquid and insoluble solid (say muddy water) is then poured into the filter paper. The liquid passes easily through the pores of the filter paper and is collected in a beaker below. This is called the filtrate. The insoluble solid particles are too large to pass through the pores and are held on the filter paper—this is called the residue.



1-2. Fig. Filtration

Rapid filtration—In many cases the process of filtration is not rapid and takes some time for completion. For quick filtration in the laboratory, a funnel with a perforated disc (usually a Buchuner Funnel), is fitted by means of a rubber cork to a filtering flask in which a partial vacuum is created by connecting it with a water-pump. A piece of filter paper is placed on the perforated disc and the mixture of liquid and insoluble solid is poured on it. The liquid passes through very quickly, under suction, leaving behind the residue on the filter paper. (Fig 1-3)

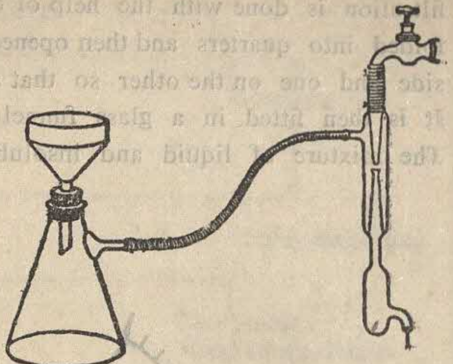


Fig. 1-3. Filtration under reduced pressure

If however the solid is soluble in water, this cannot be separated from the liquid by the above mentioned methods. In such cases the solid may be separated from the liquid by evaporating the latter slowly, when the solid is left behind as the residue.

(3) **Distillation** :—The process of distillation is useful in separating a liquid in the pure state from the non-volatile solid in solution or in suspension. In this process a volatile liquid is converted into its vapour by boiling and then the vapour is condensed back to the same liquid (called distillate) by cooling. The process of distillation is shown in the following figure (Fig 1.4). The liquid or the solution is taken in a distilling flask, fitted with a Liebig Condenser, kept in an inclined position. The other end of the condenser is introduced into a vessel, called the receiver to collect the distillate. A Liebig Condenser is a two-

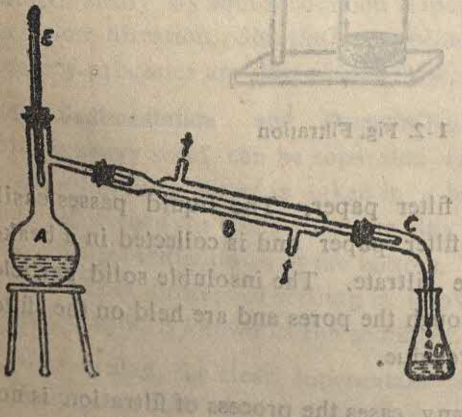


Fig. 1-4. Distillation

walled glass tube, through the annular space of which, cold water is generally circulated. On boiling the liquid (or solution) in the distilling flask, the liquid is vapourised. The vapour then passes through the inner tube of the condenser and condenses into the same liquid after coming in contact with the cold water and is collected in the receiver. The dissolved solid remains in the flask.

By this process, not only the liquid is separated from the nonvolatile solids, but the components of a mixture of missible liquids with boiling points fairly apart can also be separated. The process by which the components of a mixture of miscible liquids are separated is known as fractional distillation. The liquid mixture is taken in the distilling flask and is heated. The liquid with the lowest boiling point distils over first and is collected as the first distrillate in the receiver. When nearly whole of it has passed over, the temperature of the remaining liquid begins to rise till the temperature reaches the boiling point of another liquid which then begins to distil over and is collected as the second distillate in a second receiver. The process is continued till all the components in the liquid mixture are separated. However, to ensure complete and efficient separation, a fractionating column, (Fig 1.5) is usually inserted between the distilling flask and the condenser. The fractionating columns are so designed that a large cooling surface is exposed to the hot vapours. Vapours of higher boiling liquid will be preferentially condensed and return to the distilling flask while the vapours of more volatile liquid will pass out and are collected in the receiver after condensation. By fractional distillation

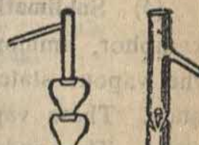


Fig. 1-5
Fractionating Column

of liquid air, its main components, Oxygen and Nitrogen can be separated.

Distillation under reduced pressure :—In some cases the liquid may decompose at its normal boiling point under one atmospheric pressure. In such cases a partial vacuum is created inside the distilling flask by connecting it with a suction pump through the condenser and the receiver. The distillation is done under reduced pressure when the liquid will boil at a much lower temperature and the decomposition of the liquid is thus avoided. Hydrogen peroxide is concentrated by distillation under reduced pressure as it is decomposed at its normal boiling point.

(4) **Sublimation** :—There are some solid substances, like iodine, camphor, ammonium chloride—which are converted directly to the vapour state by heating without passing through the liquid state. These vapours, on cooling, will condense into the same solid. The condensed solid is called the sublimate and the process of converting a solid directly into the vapour state by heating and condensing back the vapour into the original solid state on cooling is known as sublimation. The process is performed as follows.

A mixture of iodine and sand is taken in a porcelain basin and is covered by an inverted funnel, the stem of which is kept cold by wrapping it with a moist filter paper. The basin is then heated over a wire-gauze (Fig 1-6), when iodine sublimes and condenses on the inner cold surface of the funnel as a violet sublimate. The sand is left behind in the basin.

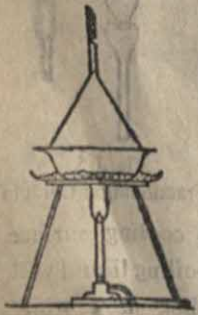


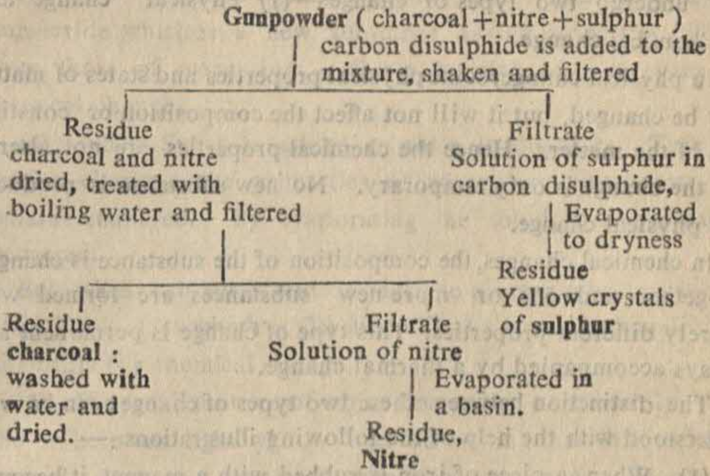
Fig. 1-6. Sublimation

There are other laboratory processes like, crystallisation, fractional crystallisation, solvent extraction etc., by which the components of a mixture can be separated and purified. These processes will be discussed in subsequent chapters.

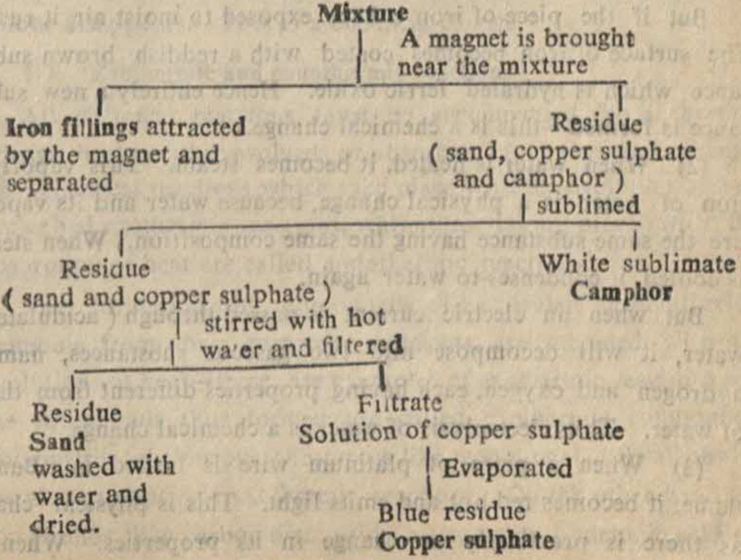
The application of the common laboratory processes to separate the ingredients of mixtures can be illustrated taking few examples.

(A) Separation of the ingredients of Gunpowder.

Gunpowder is a mixture of charcoal, sulphur and nitre (potassium nitrate). The separation is shown in the tabular form.


Gunpowder (charcoal + nitre + sulphur)
carbon disulphide is added to the mixture, shaken and filtered
Residue
charcoal and nitre dried, treated with boiling water and filtered
Filtrate
Solution of sulphur in carbon disulphide,
Evaporated to dryness
Residue
Yellow crystals of **sulphur**
Residue
charcoal : washed with water and dried.
Filtrate
Solution of nitre
Evaporated in a basin.
Residue,
Nitre

(B) Separation of a mixture of sand, copper sulphate, camphor and iron fillings.


Mixture
A magnet is brought near the mixture
Iron fillings attracted by the magnet and separated
Residue
(sand, copper sulphate and camphor)
sublimed
Residue
(sand and copper sulphate)
White sublimate
Camphor
stirred with hot water and filtered
Residue
Sand
washed with water and dried.
Filtrate
Solution of copper sulphate
Evaporated
Blue residue
Copper sulphate

1.8 Changes of Matter—physical and chemical changes : It is observed that constant changes are taking place in nature either spontaneously or by the application of external forces. Matter may undergo two types of changes—(1) Physical change and (2) Chemical change.

In physical change, some physical properties and states of matter may be changed, but it will not affect the composition or constitution of the matter. Hence the chemical properties are not altered and the change is only temporary. No new substance is produced in a physical change.

In chemical changes, the composition of the substance is changed altogether and one or more new substances are formed with entirely different properties. This type of change is permanent and always accompanied by a thermal change.

The distinction between these two types of changes can be well understood with the help of the following illustrations :—

(1) When a piece of iron is rubbed with a magnet, it becomes magnetised. This is a physical change because it will not alter the composition and hence the chemical properties of iron. The magnetic property, however, will be lost if it is heated.

But if the piece of iron is kept exposed to moist air, it rusts. The surface of iron becomes coated with a reddish brown substance which is hydrated ferric oxide. Hence entirely a new substance is formed—this is a chemical change.

(2) When water is heated, it becomes steam. This vaporisation of water is a physical change, because water and its vapour are the same substance having the same composition. When steam is cooled, it condenses to water again.

But when an electric current is passed through (acidulated) water, it will decompose into two gaseous substances, namely hydrogen and oxygen, each having properties different from those of water. Thus electrolysis of water is a chemical change.

(3) When a piece of platinum wire is heated in a Bunsen flame, it becomes red hot and emits light. This is physical change as there is practically no change in its properties. When the

platinum wire is removed from the flame, original condition is restored.

But when a piece of magnesium is heated in a Bunsen flame, it will burn with white light and produce ash. This ash is magnesium oxide which is a new substance having properties different from those of magnesium. Hence burning of magnesium is a chemical change.

(4) When Sugar is added to water it dissolves. This is a physical change as the properties of sugar, say sweet taste, still remains unaltered. By evaporating the solution, sugar can be recovered.

But when sulphuric acid is added to a sugar solution, it chars into a black mass which is Carbon. Thus a new substance is produced this is a chemical change.

(5) If a small amount of white zinc oxide is heated in a test tube it becomes light yellow and on cooling the white colour is restored, This is a physical change as no new substance is formed.

But when red mercuric oxide is strongly heated in a test tube, it breaks up into two new substances, mercury and oxygen—the red colour disappears. This is a chemical change.

1-9. Exothermic and endothermic reactions.

All chemical reactions must be accompanied by a thermal change, heat is either evolved or absorbed in a chemical change. The chemical reactions which take place with the evolution of heat are called exothermic reactions, while those taking place with the absorption of heat are called endothermic reactions.

The formation of compounds like water, carbondioxide, ammonia from their respective elements are attended with the evolution of heat—these are examples of exothermic reactions and the compounds thus formed are called exothermic compounds. Combustrin of various substances like wood, coal, oil, alcohol—are also examples of exothermic reactions. On the other hand the compounds like carbon disulphide, nitric oxide, hydriodic acid are

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formed from their elements with the absorption of heat. These are, therefore, examples of endothermic reactions and the corresponding compounds which are formed are called endothermic compounds.

In an exothermic reaction the reactants possess more energy than the products and this excess energy is evolved in the form of heat. But in an endothermic reaction, the products possess more energy than the reactants and hence some heat energy is absorbed in such reactions.

Exercises—1

1. Explain the terms : Data, Law, Hypothesis and Theory, Classify the following statements according to the above terms.

(a) All crystals are composed of atoms arranged in a regular way.
(b) Boiling point of mercury is 357°C.
(c) The moon is made of limestone.
(d) The volume of a gas varies inversely as the pressure at constant temperature.

[Ans : (a) Theory, (b) Data, (c) Hypothesis, (d) Law]

2. "Chemistry is an experimental Science"—Justify the statement.

3. What is matter ? What are the different states in which a matter can exist ? How they differ one from another ?

4. How the state of a matter changes gradually with the application of heat ? Is there any exception from this change ? Give examples.

5. What do you mean by "the boiling point of water is 100°C under one atmospheric pressure" ? Name two substances with very high and very low melting point,

6. Define and illustrate : (a) element, (b) compound and (c) mixture. Classify the following substances according to the above terms.

Glass, Petrol. Sugar, air, water, Gunpowder, Aerated water, nitrogen, Gold, diamond, sea water, iron powder, rust, common salt, milk, butter, brass, and iodine.

7. What are the chief differences between a compound and a mixture ? Explain with suitable illustrations. A heterogeneous substance must be a mixture. Is the converse always true ?—justfy with suitable example.

8. Both water and air are homogeneous substances. But water is a chemical compound whereas air is a mixture—Explain.

9. What are different types of changes that a matter may undergo ? Distinguish between them citing suitable illustrations.

10. Show whether the following changes are physical or chemical,—

(a) A piece of ice is put in a beaker of water, when the latter gets cooled :
(b) Camphor is left exposed to air and it gradually disappears.
(c) A piece of sodium floats on water, finally disappears.
(d) When electricity passes through a bulb the filament glows.
(e) When green mango ripens.
(f) Iron rod when exposed to moist air rusts.

11. How do you separate ingredients of gunpowder ?

12. What do you mean by exothermic and endothermic reactions ?—Give examples.

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CHAPTER II

LAWS OF CHEMICAL COMBINATIONS

The Chemical combinations between different elements and chemical reactions in general are found to be governed by several laws. These laws were experimentally discovered by Lavoisier and other contemporary chemists towards the end of the eighteenth century as a result of their quantitative study of chemical changes. The experimental results show that the elements never combine in any arbitrary manner, rather there exists some definite quantitative relationship among the weights of the combining elements and their products. Accordingly four laws of chemical combination by weight or Stoichiometry were formulated which describe how compounds are built up of elements. These are—

(1) The law of conservation of mass.

(2) The law of definite or constant proportions.

(3) The law of multiple proportions.

(4) The law of reciprocal proportions.

There is another law—(5) the Gay-Lussac's law of gaseous Volumes, which relats to combination of gases by Volume.

2-1. **The law of conservation of mass** : This law was experimentally arrived at by the great French Chemist Lavoisier in 1774. The law states that—

In a chemical change the total mass of the reacting substances is equal to the total mass of the products of the reaction.

This law corroborates the fact that matter is indestructible and so this is also known as the law of indestructibility of matter and forms the basis of all quantitative study in chemistry.

When any chemical change takes place, some change in the internal arrangement of the constituents particles occur leading to the formation of new substance. So in chemical changes matter may be transformed from one kind to another, but not even a minute quantity of matter is created or destroyed in the process. No change in the total mass (weight) of all the substances taking part in a chemical change has ever been observed. Though in some changes there may appear some apparent loss or gain of matter, but this is actually not the case.

Illustatrions : When coal or wood burns in air some ash is left as residue after combustion. This residue weighs much less than the original piece of coal or wood which suffered the change. Here the mass appears to be lost due to chemical change—but this is not true. Coal or wood contains carbon and hydrogen along with some non combustible materials which form the ashes. Carbon and hydrogen combine with oxygen of air during burning and produce gaseous carbondioxide and watervapour which escape into the atmosphere. Hence the apparent loss in weight is observed. If, however, all the products i.e., ash, watervapour and corbondioxide are collected and weighed, this will be exactly equal to the sum of the weights of coal or wood and oxygen with which it reacts during combustion. Thus the law of conservation of mass is not violated.

On the other hand, when magnesium is burnt or copper is strongly heated in air, the residue left actually weighs more than the original weight of the metal showing some apparent gain in mass. This occurs because oxygen of air combines with the heated metal, froming the correrponding metallic oxides and the weight of the product is increased. If we add the weight of the combined oxygen to the weight of the metal, then it will be exactly equal to the weight of the oxide produced.

The correctness of the law of conservation of mass has been demonstrated by different workers from time to time by performing various experiments, some of which are given below.

(i) *Lavoisier's experiment* :—Lavoisier was the first to formulate the law of conservation of mass and proved the accuracy of the law by his well-known experiments of the calcination of metals in air. In one of his experiments, Lavosier took a piece of metallic tin in a glass retort filled with air and its month was sealed by heating (Fig 2-1). The retort with its contents was weighed accurately in a sensitive chemical balance. The retort was then heated strongly for some times during which a part of tin was converted into white oxide of tin by reacting with oxygen of the air enclosed within the retort. When the heating was over the retort was cooled and again weighed accurately. No change in weight was observed proving that the total quantity of matter before and after the reaction remains the same. Thus the law of conservation of mass was verified.

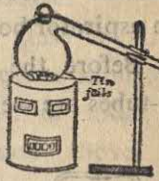


Fig. 2-1
Lavoisier's
Experiment

(ii) *Charcoal Experiment* :—In this experiment a round bottomed flask with a tightly fitted rubber stopper is taken (Fig 2-2). Through the stopper two copper wires are introduced into the flask. At the end of one there is a copper spoon on which a piece of 'charcoal is taken. A platinum wire connects the two copper wires touching the charcoal piece on the spoon. The flask is then filled with oxygen and weighed accurately. By connecting the copper wires to the two terminals of a battery an electric current is passed through the platinum wire, which becomes red hot and ignites charcoal which burns completely and produces carbondioxide gas leaving little or no residue. The flask is then cooled to room temperature and weighed again, which remains unaltered. This proves the indestructibility of matter and establishes the correctness of the law.

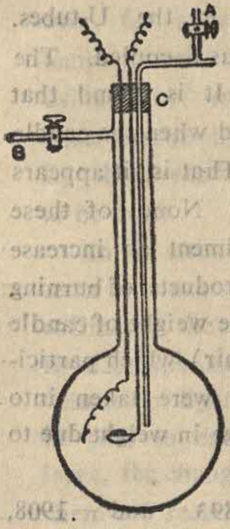


Fig. 2-2.
Charcoal Experiment

(iii) *Candle experiment* :—When a candle burns in air, it gradually disappears, practically leaving nothing. Matter is thus appeared to be destroyed. But this inference is really erroneous and only apparent. This would be obvious if the burning of candle be carried out in the following arrangement.

Experiment : A candle is placed on perforated cork at the bottom of a glass chimney. The top of the chimney is fitted with a cork carrying a tube which is connected serially to two U-tubes containing solid caustic potaph in one tube and anhydrous calcium chloride in the other. The system is finally connected to an aspirator bottle filled up with water, (Fig 2-3)

Before the experiment, the chimney together with the two U-tubes are weighed. The candle is then lighted, the cork quickly replaced and the aspirator bottle opend. Air enters the chimney through the perforations in the bottom cork and the candle continues to burn producing two gases, carbondioxide and water-vapour. On passing out, these gases are absorbed in the U-tubes. After sometime, the candle is put off, the apparatus is cooled. The chimney with the U-tubes are weighed again. It is found that instead of a loss of weight apparantly observed when the candle burns, there is actually an increase in weight. That is, it appears that when candle burns, matter is created. None of these inferences are, however, true. In this experiment an increase in weight has been observed because both the products of burning have been weighed, but before burning only the weight of candle was taken ignoring the weight of oxygen (from air) which participated in the burning. If the weight of oxygen were taken into account, then there would have been no change in weight due to burning. This proved the validity of the law.

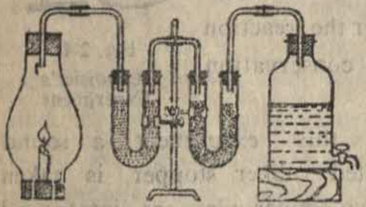


Fig. 2-3 The Candle Experlment

(iv) *Landolt*'s *experiment* :—Between 1893 and 1908, Landolt carried out a series of expriments in order to test the truth of the law of conservation of mass. He performed experiments with fifteen chemical reactions in which the evolution of heat is small, of which the following may be given as examples :

1. Solutions of hydriodic acid and of iodic acid were mixed to yield water and a precipitate of iodine.

2. Solutions of ferrous sulphate and of silver sulphate were mixed to yield a solution of ferric sulphate and a precipitate of of metallic silver.

3. Solutions of iodine and sodium sulphite were mixed to yield a solution of sodium sulphate and sodium iodide.

The reactions were carried out in a H-shaped glass apparatus (Fig 2-4), into one limb of which Landolt placed a solution of hydriodic acid and in the other he took a solution of iodic acid in order to perform the first reaction mentioned above. The ends of the two limbs were then sealed to prevent any loss of materials. The apparatus was accurately counterpoised on a balance sensitive to 1 part in 10, 000, 000. The two solutions were then mixed by tilting the apparatus when the reaction took place. After the reaction was over, the apparatus was cooled to room temperature and weighed in the same balance using the same counterpoise. Landolt observed that the weight remained unchanged. By these experiments the law was shown to be exact.

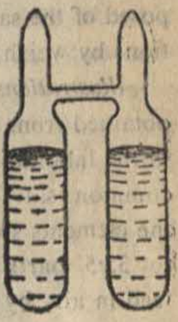


Fig. 2-4
Landolt's Experiment

In the strictest sense the law of conservation of mass does not seem to be exact, as mass and energy are inter convertible. According to Einstein the evolution of heat energy E in a chemical change should be accompanied by a loss of mass equal to E/C^2, where C is the velocity of light. Matter is therefore now regarded as convertible in part to energy during a chemical process. Since C is very large, the change of mass due to liberation of energy in ordinary chemical reactions is extremely small. The combusition of 1 gram atom, i.e., 12 grams of carbon, for example, liberates 94000 calories of heat, the corresponding loss of mass will be equal to $4{\cdot}32 \times 10^{-9}$ gram, which is too small to be measured with the most sensitive balance. The law of conservation of mass as phrased above, therefore, remains a correct statement of experimental fact. In nuclear reactions, however, where enormous amount of energy is released, the loss of mass should be taken into account. Hence, if absolute precision is required, it may be stated that *the sum of the quantity of matter and the energy in an isolated system is always constant.*

2-2. The Law of constant or definite proportions :

The law was formulated by French chemist Proust in 1797 which states that—

A given chemical compound always contains the same elements united in the same fixed proportions by weight.

This law implies that, whatever be the source or the method of preparation of a chemical compound, if it is pure, it must be composed of the same elements combined in the same definite proportions by weight.

Illustrations : Take for example, common salt. It can be obtained from sea water or from dried up lakes or can be prepared in the laboratory by different methods. If all the varieties of common salt are analysed, it is found that common salt contains the elements sodium and chlorine only, always in the ratio of 23 to 35·5 parts by weight. Lead monoxide can be made by heating lead in air, by heating lead carbonate, or by heating lead nitrate. Whichever mode of preparation is used, it is invariably found that in every sample 100 grams of lead are combined with 7·721 grams of oxygen.

Experiments to verify the law :

The law may be verified by analysing the same compound prepared by diffarent methods. Some illustrations are given bellow.

(a) *The analysis of black cupric oxide*—

Different samples of black oxide of copper are prepared by the following methods—

(*i*) by heating strongly green copper nitrate.

(*ii*) by heating strongly blue copper carbonate.

(*iii*) by heating strongly blue copper hydroxide.

In every case these compounds are decomposed on strong heating to yield black cupric oxide.

Now, one gram of each of the three samples of copperoxide are taken in three porcelain boats (one sample in each boat) which are placed one after another in a combustion tube (Fig 2-5). The boats are heated strongly in a stream of dry and pure hydrogen gas, when black cupric oxide is reduced to red metallic copper in each boat. When the reduction is complete, boats are cooled in a slow stream of hydrogen in the tube and are separately weighed in a balance to find out the weight of metallic copper left in each boat. It is found that in each boat 0·798 gram of copper is formed. The weight of oxygen in 1 gram each of the samples of cupric oxide is therefore ·202 gram. This means that different samples of copper oxide contains copper and oxygen in the ratio of 63·57 to 16 parts by weight, ie, it has a constant composition. This proves the truth of the law of constant proportions.

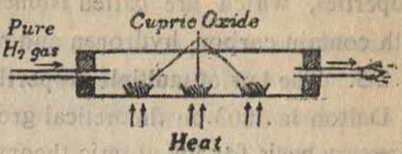


Fig. 2-5 Analysis of cupric oxide

(b) The law received accurate confirmation by the precise experimental work of Stas (1860). Among many other experiments he prepared silver chloride from purified materials in four different ways. He found that 100 grams of silver yielded 132·843, 132·848, 132·842, 132·849 grams of silver chloride in each method of preparation. Hence, within the limits of experimental error, the law of constant proportion is regarded as completely established.

N.B. (i) Exception to the law of constant proportions are however, observed when isotopes of an element take part in the formation of a given compound. Thus carbon dioxide formed with ^{12}C atoms and with ^{14}C atoms would lead to different proportions of carbon and oxygen by weight. Of course, such variation in composition is very rarely met with, as the relative proportions of the various isotopes in any compound remain more or less the same. As a result the composition of the compound by weight remains practically unaltered and the law of constant proportions generally holds good. (2) The law of constant proportions implies that a particular compound has a fixed and constant composition, but the converse of this idea may not be always true. Sometimes it is found that the same elements combine in the same weight-ratio to form different compounds each with characteristic properties, which are called isomers. Thus glucose and fructose both contain carbon, hydrogen and oxygen in the same ratio.

2-3. The law of multiple proportions : The law was proposed by Dalton in 1803 on theoretical grounds ; he saw that it was a necessary basis for his atomic theory. The law states that :

When two element combine to form more than one compound the weights of one elements which unite with a given weight of the other, bear a simple ratio to one another ie, are in the ratio of small whole numbers.

If two elements *A* and *B* combine to form two different compounds *P* and *Q*, then the weight-ratios of *A* and *B* in the two compounds would be different. Suppose in *P* ; 1 gram. of *A* combines with *x* gram. of *B*, and in *Q*, 1 gram. *A* combines with *y* gram of *B*, then, the law suggests that the ratio $x : y$ will be a simple ratio.

Illustrations :—(1) Hydrogen and oxygen combine to form two compounds, water and hydrogen peroxide. On analysis it is found that 1·008 grms of hydrogen combine with 8 grms. of oxygen in water and with 16 grms of oxygen in hydrogen peroxide. Thus, the weights of oxygen which unite with the same weight of hydrogen (i.e., 1·008 grm.) bear to each other the ratio 8 : 16 or 1 : 2, which is a simple ratio.

(ii) The law is best illustrated by the composition of five oxides of nitrogen. On analysis, it has been fouud that the ratio of the weights of nitrogen to oxygen in these compounds are as follows :—

Oxides of nitrogen	Composition by weight	
	Nitrogen :	Oxygen
Nitrons oxide, N_2O	14 :	8
Nitric oxide, NO	14 :	16
Nitrogen trioxide, N_2O_3	14 :	24
Nitrogen tetroxide, N_2O_4	14 :	32
Nitrogen pentoxide, N_2O_5	**14 :**	**40**

∴ the different weights of oxygen combining with a defiinite weight (14 grms) of nitrogen are in the ratio of 8 : 16 : 24 : 32 : 40 or, 1 : 2 : 3 : 4 : 5

(iii) The analysis of four hydrides of carbon, namely methane, ethane, ethylene and acetylene also illustrate the law. The hydrides have the following proportions of carbon and hydrogen by weight :—

Compound	Composition by weight carbon : hydrogen
Methane, CH_4	12 : 4 × 1·008
Ethane, C_2H_6	12 : 3 × 1·008
Ethylene, C_2H_4	12 : 2 × 1·008
Acetylene, C_2H_2	12 : 1 × 1·008

So, the different weights of hydrogen which unite with a fixed weight of carbon (12 grm) are in the simple ratio of 4 : 3 : 2 : 1.

Many other similar illustrations will help to uphold the truth of the law.

Experiment to verify the law :—

The following experiment can easily be done in the laboratory to establish the truth of this law.

Known amounts of black cupric oxide (say a grm) and red cuprous oxides (say *b* grm) are taken in two porcelain boats which are introduced in a hard glass tube as in Fig 2-6, The boats are then strongly heated in a current of dry hydrogen gas for sometime, when both the oxides will be converted into metallic copper. The apparatus is then cooled and the two boats are weighed again and the amounts of copper produced in the two cases are noted.

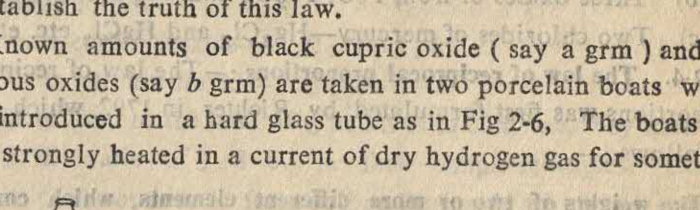


Fig.-26 Expl, to verify the law of multiple proportions.

Calculations :—(i) *Cupric oxide*

Let 'a' grms of cupric oxide produces 'x' grms of copper

∴ x grm of copper units with $(a-x)$ grms of oxygen.

(2) *Cuprous oxide* :

Let 'b' gm, of cuprous oxide produce 'y' gm of copper

∴ y gm of copper units with $(b-y)$ gm of oxygen.

Hence x gm. of copper units with $\frac{(b-y)\times x}{y}$ gms of oxygen.

The ratio of the weights of oxygen which combine with x gms of copper is thus $(a-x) : \frac{(b-y)\,x}{y}$.

From the above experiment, this ratio was actually found to be 2 : 1, which is a simple ratio.

In a similar manner, this law may be experimentally verified by the chemical analysis of other compounds, e. g.,

(a) Two oxides of carbon, carbon monoxide and carbon-dioxide.

(b) Three oxides of iron, FeO, Fe_2O_3 and Fe_3O_4.

(c) Two chlorides of mercury—Hg_2Cl_2 and $HgCl_2$ etc. etc.

2-4. **The law of reciprocal proportions** :—The law of reciprocal proportions was first formulated by Richter in 1792, which states as follows :—

The weights of two or more different elements, which combine seperately with a definite weight of another element, are either the same as, or simple maltiples of the weights in which these different elements combine with one another.

The statement of the law implies that, if 'a' grams of an element A and 'b' gram of another element B combine separately with 'c' grams of a third element C to form two different compounds, then, when A and B will combine with each other, they will do so in the weight ratio $a : b$ or in a simple multiple of this ratio, i.e., $2a : 3b$ or $a : 3b$ or $ma : nb$ where m and n are small whole numbers.

Illustrations : –

(*i*) Hydrogen and oxygen combine with carbon separately to form methane and carbondioxide. They also combine with each other.

In methane : 12 grams of carbon are combined with 4 grams of hydrogen.

In carbondioxide : 12 grams of carbon are combined with 32 grams of oxygen.

According to the law, the proportions by weight of hydrogen and oxygen respectively in all compounds of these two elements should be equal to the ratio $4m : 32n$ where m and n are two small whole numbers.

In water : 4 grams of hydrogen combine with 32 grams of oxygen, and $m=n=1$; in hydrogen peroxide 4 grams of hydrogen combine with 64 grams of oxygen, and $m=1$, $n=2$.

(ii) Carbon and sulphur separately combine with oxygen to yield carbon dioxide and sulphur dioxide respectively. On analysis the weight ratio of the elements in these compounds are found to be—

in carbondioxide— $C : O = 3 : 8$
in sulphurdioxide— $S : O = 8 : 8$

According to the law, if C and S is to combine, they must do so in the ratio of 3 : 8 or in their simple multiples. Carbon and sulphur combine to form carbondisulphide which on analysis shows that the ratio of the weights of carbon and sulphur is equal to 3 : 16 ; 16 is a simple multiple of 8. Hence the validity of the law is established.

The law of reciprocal proportions is a special case of the law of equivalent proportions. This can be understood in the following way. If some of the binary compounds of oxygen are studied, it is found that :

8 grams of oxygen combine with,

35·457	grams of chlorine
20	grams of calcium
1·008	grams of hydrogen and so on.

According to the law of reciprocal proportions, the elements on the right hand side shall combine, if they combine at all. with one another in proportions of the weights shown or in simple multiples of them. But the number of parts by wt. of an element which combine with 8.00 parts by weight of oxygen is known as its equivalent. This will be discussed more fully in subsequent chapter. Hence the elements combine in the ratio of their equivalents or in simple multiples of them—this is the law of equivalent proportions.

2-5. Gay Lussac's Law of Gaseous-volumes :

All the four laws of chemical combination mentioned above relate to combination of substances by weight. It was, however, observed that, if the reaction takes place between gaseous substances, there exist some volume-relationship of the reacting gases. Cavendish as well as Lavoisier observed from their experiments that 50 c.c. of oxygen combine with 100 c.c. of hydrogen to produce water, that is, hydrogen and oxygen combine in the ratio of 2 : 1 by volume. The French scientist Gay-Lussac, however, studied systematically different gaseous reactions and showed that there exist in every case a simple relationship between the volumes of the reacting gases and also those of the gaseous products. In 1808 Gay Lussac made a generalised formulation of this fact. This is known as the law of gaseous volumes or Gay-Lussac's Law. The law states :—

The volumes of gases taking part in a chemical reaction bear a simple numerical relation to one another and also to the product, if gaseous, if all measurements are made under the same conditions of temperature and pressure.

The law may be illustrated by the following reactions—

(a) One volume of hydrogen and one volume of chlorine yield two volumes of hydrogen chloride (ratio of volumes 1 : 1 : 2)

(b) Two volumes of hydrogen and one volume of oxygen yield two volumes of steam (ratio of volumes 2 : 1 : 2)

(c) One volume of nitrogen and three volumes of hydrogen yield two volumes of ammonia (ratio of volumes 1 : 3 : 2)

(d) One volume of methane and two volumes of oxygen yield one volume of carbondioxide and liquid water. (ratio of volumes 1 : 2 : 1)

It should be noted that the law describes all reactions in which gases take part, even though solids or liquids are also reagents or products.

Numerical problems :—

1. On analysis, two samples of silver chloride give the following results :

Sample (a) 12·1499 gms of silver chloride give 9·146 gms of silver.

Sample (b) 69·6558 gms of silver chloride give 52·423 gms of silver.

Show that the results are in agreement with the law of constant proportions.

In sample 'a' : 12·1499 gms of silver chloride give 9·146 gms of silver,

∴ the weight of chlorine = 12·1499 − 9·146 = 3·0039 gms.

$$\therefore \frac{\text{weight of silver}}{\text{weight of chlorine}} = \frac{9{\cdot}146}{3{\cdot}0039} = 3{\cdot}044.$$

In sample 'b' : 69·6558 gms of silver chloride give 52·423 gms of silver.

∴ the weight of chlorine = 69·6558 − 52·423 = 17·2328 gms.

$$\therefore \frac{\text{weight of silver}}{\text{weight of chlorine}} = \frac{52{\cdot}423}{17{\cdot}2328} = 3{\cdot}042.$$

Thus in the two samples of silver chloride, the ratio of the weights of silver to chlorine is practically the same. Hence the results are in agreement with the law of constant proportions.

2. Three oxides of nitrogen contain 30·43, 46·67 and 63·68 percent of nitrogen. Show clearly that the law of multiple proportions holds.

In the first oxide : 30·43 gms of nitrogen combine with (100 – 30·43) = 69·57 gms of oxygen.

∴ 1 gm of nitrogen combine with $\frac{69 \cdot 57}{30 \cdot 43} = 2 \cdot 286$ gms of oxygen.

In the second oxide :

46·67 gms of nitrogen combine with (100 – 46·67) = 53·33 gms of oxygen.

∴ 1 gm of nitrogen combine with $\frac{53 \cdot 33}{46 \cdot 67} = 1 \cdot 143$ gams of oxygen.

In the third oxide :

63·68 gms of nitrogen combine with (100 – 63·68) = 36·32 gms of oxygen.

∴ 1 gm of nitrogen combine with $\frac{36 \cdot 32}{63 \cdot 68} = \cdot 57$ gm of oxygen.

The different weights of oxygen combining with a fixed weight of nitrogen (i.e. 1 gm) are in the ratio of 2·286 : 1·143 : ·571 i.e. 4 : 2 : 1 which is a simple ratio. Hence the results show clearly that the law of multiple proportions holds.

3. A metal *M* gives two oxides. On heating 1 gm of each in a current of hydrogen, 0·12585 gm and 0·2264 gm of water are found respectively.

(i) Show the results are in agreement with the law of multiple proportions.

(ii) If the formula for the latter oxide be *MO*, find that of the other.

18 gms of water contain 16 gms of oxygen.

∴ 0·12585 gm of water contains $\frac{16}{18} \times \cdot 12585 = 0 \cdot 119$ gm of oxygen, This 0·1119 gm of oxygen comes from 1 gm of **first oxide**, and hence in 1 gm of first oxide $M=(1-\cdot1119)=0\cdot8881$ gm., and $O=0\cdot1119$ gm.

Again, 0·2264 gm of water contain $\frac{16}{18}\times0\cdot2264=0\cdot2013$ gm of oxygen.

∴ in 1 gm. of the **second oxide**

$M=(1-\cdot2013)=0\cdot7987$ gm. and $O=0\cdot2013$ gm.

(i) In the second oxide, ·8881 gm of M combines with

$\frac{\cdot2013}{\cdot7987}\times\cdot8881=0\cdot2238$ gm of oxygen

and in the first oxide, ·8881 gm of M combines with 0·1119 gm of oxygen

∴ the wts. of oxygen which combine with the fixed wt. of the metal (i.e., ·8881 gm) are in the ratio of ·1119 : ·2238 i.e., 1 : 2. Hence the results are in agreement with the law of multiple proportions.

(ii) The formula of the second oxide is MO, i.e.,

$$\frac{\text{Number atoms of } M}{\text{Number atoms of } O}=\frac{1}{1}=\frac{0\cdot7987/x}{0\cdot2013/16}$$

Where x = atomic weight of M, and 16 = atomic wt. of oxygen.

$$\therefore\ x=\frac{0\cdot7987}{0\cdot2013}\times16=63\cdot49.$$

In the first oxide : $\frac{\text{Number of atoms of } M}{\text{Number of atoms of } O}=\frac{0\cdot8881/63\cdot49}{0\cdot1119/16}=\frac{2}{1}$

∴ the formula of the frist oxide is M_2O.

4. State how the results given below illustrate a law of chemical combination. Enunciate the law.

(a) 0·46 gm. of magnesium produces 0·77 gm. of magnesium oxide.

(b) 0·82 gm. of magnesium liberates 760 cc. of hydrogen at N.T.P. from an acid.

(c) 1·26 gm. of water result from the union of 1·12 gms. of oxygen with hydrogen.

From (a) ·46 gm. of magnesium combine with $(\cdot 77 - \cdot 46) = \cdot 31$ gm of oxygen.

From (b) ·82 gm. of magnesium liberates 760 c.c. of hydrogen at N.T.P. from an acid.

ie, ·82 gm. of magnesium liberate $760 \times \cdot 00009 = 0\cdot0684$ gm. of H_2 (∵ 1 c.c. of hydrogen at NTP weighs ·00009 gm.).

Or, ·46 gm. of magnesium liberates $\frac{\cdot 0684 \times \cdot 46}{\cdot 82} = 0\cdot0384$ gm. of hydrogen

∴ the weights of oxygen and hydrogen that combine with and displaced by the fixed wt. of magnesium (i.e., .46 gm) are in the ratio of of 0·31 : 0·0384 or, 8·07 : 1

Now from (c) 1·12 gm of oxygen unite with $(1\cdot26 - 1\cdot12) = 0\cdot14$ gm of hydrogen.

∴ the wts of oxygen and hydrogen which unite to form water are in the ratio of 1·12 : 0·14 i.e., 8 : 1, which is practically the same as the ratio of their wts (8·07 : 1) when seperately combine with or displaced by another element i.e., magnesium. Hence the results illustrate the law of reciprocal proportions. The law states as follows :—

The weights of two or more different elements, which combine seperately with a definite weight of another element, are either the same as, or simple multiples of the weights in which these different elements combine with one another.

5. Ferreous sulphide contains 63·53%of iron and 36·47% of sulphur. When 2 gms of iron is heated with 6 gms of sulphur, how much ferrous sulphide is formed and how much sulphur remains unchanged.

63·53 gms of iron combine with 36·47 gms of sulphur.

∴ 2 gms of iron combine with $\frac{36\cdot47 \times 2}{63\cdot53} = 1\cdot148$ gms of sulphur.

∴ amt. of sulphur remains unchanged $= 6 - 1\cdot148 = 4\cdot852$ gms and the amount of ferreous sulphide formed $= 2 + 1\cdot148 = 3\cdot148$ gms.

Exercise 2

1. State the law of conservation of mass and verify it with a suitable example.

2. Do the following observations contradict or not the law of conservation of mass ?—Explain,

(a) Naphthalene balls kept in an almirah disappears gradually.

(b) A piece of iron kept exposed to moist air rusts and increases in weight.

(c) A piece of coal when ignited burns away leaving a small quantity of ash.

3. State and explain wtth suitable example the law of constant proportions. Is the converse statement of this law true ? Explain with examples.

4. Calcium chloride, a compound of calcium and chlorine, contains 64·0% chlorine. How much calcium chloride have to be decomposed to produce 200 gms of calcium metal ? [555·55 gms.]

5. 0·7 gm. of iron unite directly with 0·4 gm of sulphur to form ferreous sulphide. If 2·8 gm. of iron are dissolved in dilute hydrochloric acid and excess of sodium sulphide solution is added, 4·4 gms. of ferreous sulphide will be precipitated. Show that the results agree with the law of constant proportions.

6. State and explain the law of multiple proportions. Verify the law using the compounds of carbon and oxygen.

7. (i) Carbon forms two gaseous hybrides containing 75% aud 80% of carbon respectively. Show that these compositions accord with the law of multiple proportions.

(ii) A metal forms two chlorides containing respectively 65·6% and 65·9% of chlorine. Show that these figures are in accordance with a law of chemical combination. State the law.

8. State the law of reciprocal proportions and explain the law with a suitable example. Why this law is also called the law of equivalent proportions ?

9. (i) Ammonia contains 17·65% hydrogen, water contains 11·11% hydrogen and nitrogen trioxide contains 36·84% nitrogen. Show that these results illustrate the law of reciprocal proportions.

(ii) Potassium chloride contains 52·5% potassium, potassium iodide contains 23·6% potassium and iodine chloride contains 78·2% iodine.

Show whether these figures accord with the law of reciprocal proportions.

10. Two oxides of a metal M contain 27·6 and 30·0 percent of oxygen respectively. If the formula of the first be M_3O_4, find that of the second. [M_2O_3]

11. State and illustrate the Gay-Lussac's law of gaseous volumes with three examples.

CHAPTER III

CONSTITUTION OF MATTER : DALTON'S ATOMIC THEORY

The laws of chemical combination definitely establish the fact that there exist distinct quantitative relationship between the weights of the combining elements. The theoretical explanation of such relation requires the basic concept of the ultimate constitution of matter, i. e., how and of what the matter is constituted. The opinion that substances are not ultimately uniform and homogeneous, but consist of a vast number of minute indivisible particles, was held by many early philosophers and thinkers like the great Indian sage Kanad, the Greek philosophers Leukippus (C 500 B. C.), Democritus (C 450 B. C.) and Lucretius (57 B. C.). Greeks used to call these particles—atoms [from Greek a tome, meaning not divisible]. This opinion was also put forward by many Scientific thinkers in the seventeenth and eighteenth centuries. Isaac Newton (1675) suggested that chemical change resulted from the separations and new associations of permanent particles. It remained, however, for John Dalton (1803) to develop this metaphysical idea about the structure of matter into a scientific theory in order to give a quantitative interpretation of the laws of chemical combination.

3-1. **Dalton's atomic theory :**—The main postulates of Dalton's atomic theory are as follows :—

(i) Matter is discrete and is composed of minute indestructible particles called atoms, which are not subdivided in the course of chemical change.

(ii) Atoms of the same element are similar to one another in all respects and are equal in weight.

(iii) Atoms of different elements have different properties and differ in weight.

(iv) Chemical combination between two or more different elements takes place by the union of the atoms of these elements in simple numerical proportions, viz 1 : 1 ; 1 : 2 ; 2 : 3 ; etc.

It is the last or the fourth postulate which contains Dalton's original and significant contribution of chemical theory and which helps us to explain the facts of chemical combination. According to Dalton, the atom, therefore, is the smallest particle of an element which can enter into, or be expelled from, chemical transformation.

3-2. Critical Survey of Dalton's Atomic Theory.

Dalton formulated his famous atomic theory with bold speculations and careful deductive reasoning which has a great practical value and contributed much towards the development of chemical researches in the nineteenth century. But there are certain drawbacks in the assumptions of the atomic theory which has made it insufficient to explain some facts. Consequently, it has to be modified particularly in the light of new discoveries made in later years. Some of the limitations of the theory are mentioned below :

Limitations of theory—(i) Dalton, in his assumption, considered atoms to be the smallest particles of all kinds of matter, be it an element or a compound. He referred to the smallest particles of an element as 'simple atom' and that of the compound as 'compound atom' only to distinguish between them. This concept of 'compound atom' was not found tenable and it was found later by Avogadro (1811) that this idea of 'compound atom' has to be replaced by that of 'molecule'—which was considered to be the smallest particle of matter that can exist in the free state. The distinction between 'atom' and 'molecule' will be explained in the next section.

(ii) Dalton assumed that each atom has a definite weight, but it was difficult to determine even the relative weights of the atoms from his concept. Dalton asserted that the combining weight of an element was its atomic weight and assumed that if two elements combine to form only one compound, they should unite in the simplest ratio of their atoms, i.e., it was formed of one atom of each element. Thus according to Dalton, water was formed by the combination of one hydrogen atom and one oxygen atom, which obviously corresponds to its formula HO. The atomic weight of oxygen would then be equal to 8 taking that of hydrogen to be one. Berzelius, however, showed that the atomic weight of oxygen should be 16 instead of 8.

(iii) Some ideas of Dalton have been found to be incorrect in the light of modern discoveries. It is now definitely established that atom is not the smallest particle of matter, there are subatomic particles, like protons, neutrons, electrons etc., which constitute the atom. Hence the Dalton's concept of indivisibility of atom is not correct.

(iv) The discovery of isotopes has proved that atoms of the same element, though similar in properties may have different weights. Similarly the existence of isobars has changed the Dalton's idea that the atoms of different elements, though are different in properties, may not always differ in weight.

3-3. **Modification of Dalton's atomic theory**: Some very startling discoveries were made in the beginning of the present century. The informations obtained from these discoveries has helped to modify and expand the Dalton's atomic theory, without, however, changing its basic structure. The fundamental assumptions of the atomic theory may thus be altered in the following way—

(i) Atoms are the smallest units of matter which take part in a chemical reaction and are not divisible in such changes. Atom, however, can be broken down into subatomic particles like protons, neutrons, electrons, etc. by applying sufficient energy thereby losing its identity.

(ii) Atoms of the same element have similar properties but are not necessarily all indentical in weight. An element may have isotopes which differ in weights.

(iii) Atoms of different elements have different properties but they do not necessarily always differ in weights. Isobars are the atoms of different elements possessing same atomic weight.

(iv) Atoms of different elements combine chemically in simple numerical proportions to produce molecules of new substances.

3-4. The atomic theory and stoichiometric laws :

Though the basic assumptions of Dalton's atomic theory have subsequently been modified, but the theory has been successfully utilised to explain the laws of chemical combination by weight which are all based on experiments. The explanations of the laws of stoichiometry in the light of the atomic theory are given below :

(i) The Law of Conservation of mass :—The total mass of a chemical system must be equal to the sum of the masses of all the atoms present in it. During chemical reaction, combination or separation of these atoms take place. In such regrouping of atoms, the total number of atoms remain constant because atoms cannot be destroyed or created. Since each atom has a definite mass, total mass of the system remains unaltered and constant in a chemical reaction. Hence the law.

(ii) The Law of Definite Proportions :—According to Dalton's atomic theory, atoms of the reacting substances combine in simple and constant ratio to form the 'compound atom's (i.e., molecules) of the products. Let x atoms of an element A unite with y atoms of another element B to form the molecule of the componnd C. Let a and b be the atomic weights of the elements A and B respectively. Therefore, in every molecule of the compound C, the ratio of weights of A and B is $x \times a : y \times b$. If there are n molecules in a given quantity of the compound C, then

$$\frac{\text{weight of } A}{\text{weight of B}} = \frac{x \times n \times a}{y \times n \times b} = \frac{x \times a}{y \times b} = \text{constant},$$

because, according to the atomic theory, the atomic weights a and b are constant and the ratio $x : y$ is also fixed for the compound C. That is the compound C has a fixed and definite composition by weight. Hence the law of definite propotions is explained.

(iii) The Law of Multiple Proportions :—Let the two elements A and B combine to produce two or more compounds. According to Dalton's atomic theory, the molecules of these compounds must contain different number of atoms of A and B which unite in simple numerical proportions. Let the formula of these compounds be $A_x\, B_y\, A_m\, B_n$ and $A_p\, B_q$, where the ratio of the number of atoms of A and B in these compounds are $x : y$, $m : n$ and $p : q$ respectively—all of them are small integers. If a and b are the atomic weights of the elements A and B, the proportions by weight of the elements A and B in these compounds are—

Compound	weight of A : weight of B.
$A_x\, B_y$	$ax : by$ or $a : \frac{by}{x}$
$A_m\, B_n$	$am : bn$ or $a : bn/m$
$A_p\, B_q$	$ap : bq$ or $a : bq/p$.

Therefore the different weights of B that combine with a fixed i.e. a part by weight of A are in the ratio of $\frac{by}{x} : \frac{bn}{m} : \frac{bq}{p}$ or, $ymp : xnp : xmq$, which must be a simple ratio as x, y, m, n, p, q are all small integers. Thus the law follows from Dalton's Atomic Theory.

For example, let us consider three oxides of nitrogen. Taking nitrous oxide, N_2O, to be $A\ B_y$, $x=2$, $y=1$, nitric oxide, NO to be A_mB_n, $m=1$, $n=1$ and nitrogen dioxide, NO_2 to be A_pB_q, $p=1$, $q=2$, the above ratio $ymp : xnp : xmq$ becomes $1 : 2 : 4$, which is a simple ratio.

(iv) The Law of Reciprocal Proportions :—This law also can be explained by the atomic theory. Let an element A combine separately with two other elemens B and C to form the compounds A_xB_y and A_pC_q, where x atoms of A combine with y atoms of B in the first compound and p atoms of A combine with q atoms of C in the second compound. Let us also consider that the elements B and C combine between themselves in the atomic ratio of $m : n$ to form the compound B_mC_n. According to Dalton, x, y, p, q, m, n are all small integers. If a, b and c are the atomic weights of A, B and C respectively, the ratio of the weights of different elements in these compounds are as follows :—

Compound	ratio of the wts of the constituent elements
A_xB_y	$ax : by$ or $a : \frac{by}{x}$.
A_pC_q	$ap : cq$ or $a : \frac{cq}{p}$.
B_mC_n	$bm : cn$.

Let $\frac{by}{x}=k$, and $\frac{cq}{p}=l$. Since k and l are the weights of B and C which separately combine with a definite weight, *i.e*, a parts by weight of A, then according to this law, they should combine between themselves either in the same ratio of $k : l$ or in simple multiple of this ratio, where $\frac{k}{l}=\frac{by}{x}\div\frac{cq}{p}=\frac{byp}{cqx}$.

Now, in the compound B_mC_n, the ratio of the weights of B and C is $\frac{bm}{cn}$ or $\frac{bm\times pqxy}{cn\times pqxy}$ or $\frac{byp}{cqx}\cdot\frac{mqx}{npy}=\frac{k}{l}\cdot\frac{mqx}{npy}$.

Hence $\frac{bm}{cn}$ is either equal to $\frac{k}{l}$ (where $mqx=npy$) or simply related to it as both mqx and npy, being the products of small integers, are small whole numbers. Thus the law is explained.

For example, let us consider the following three compounds : carbondioxide CO_2, carbondisulphide CS_2 and sulphurdioxide SO_2. Taking CO_2 as A_xB_y, $x=1$, $y=2$, CS_2 as A_pC_q, $p=1$, $q=2$ and SO_2 to be B_mC_n, $m=1$, $n=2$, we find $mqx=2$ and $npy=4$.

$\therefore\ \frac{bm}{cn}=\frac{2k}{4l}$ or $\frac{k}{2l}$. which is simply related to k/l.

Thus all the four laws of chemical combination by weight have been clearly explained and deduced from Dalton's Atomic Theory. But difficulty arises when it is used to explain the law of gaseous volume and it is found that this theory alone cannot explain Gay-Lussac's Law. This will be discussed in the next chapter.

3-5. Concepts of atoms and molecules :—

It has already been stated that, Dalton, in his atomic theory, did not distinguish clearly between the smallest particle of an element and that of a compound. In order to explain the differences in the constitution of elements and compounds, the concepts of atoms and molecules have been visualised.

Consider an element, say a piece of iron. If it is divided and subdivided, we get very small particles of iron possessing the same properties as those of the original metal. If this process of division continues we shall come to a state when these tiny particles still have the properties of iron, but which cannot be further divided retaining its properties. Such minute particles are called 'atoms'. Hence we can say, a piece of iron is an aggregate of extremely large number of iron atoms. So also the case with other elements like, gold, silver, mercury, carbon and so on. The atoms of differnt elements will combine chemically producing a compound. Hence atom may be defined in the following way :—

An atom is the smallest particle of an element possessing all its properties which can take part in a chemical change, without being altered in any way.

There are many elements, atoms of which cannot exist in the free state. Two or more atoms combine to form a small particle, which remain in the free state retaining all the properties of the element. Such minute particles are called molecules. Take for example, the gaseous elements like hydrogen, oxygen, nitrogen and so on. Two atoms combine to form molecules of each of these elements. Phosphorus and arsenic molecules consist of four atoms. However in case of many metallic elements, as well as inert gases like Helium, Argon etc. the molecules contain only one atom i.e., atoms are capable of remaining in the free state and in these cases, atoms and molecules are the same. Hence we can say the *molecules are the smallest particles of an element which can remain in the free state possessing all its properties*—only exceptions are the monoatomic elements, i.e., whose molecules contain only one atom. An element is therefore an aggregate of molecules and molecules are formed from atoms.

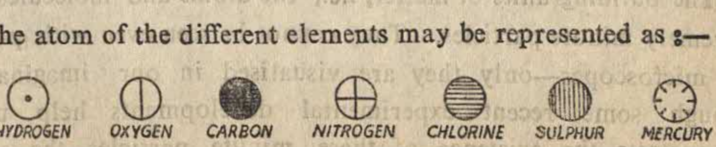
Now let us see how compounds are constituted. Consider a piece of chalk which is a compound. If this piece of chalk is divided and subdivided into smaller and smaller parts, we may reach a particular state, when the minute particles thus produced will possess all the properties of chalk. These are the molecules of chalk. If we try to divide these minute particles further, the molecules of chalk will break down into atoms of three elements, calcium, carbon, and oxygen from which it is made, losing the properties of chalk. Hence the piece of chalk is consituted by the aggregation of very large number of chalk molecules. So also the other compounds—water for example is composed of water molecules – which posses all the properties of water and each is formed by the combination of 2 atoms of hydrogen and one atom of oxygen. Hence water molecules, are tri-atomic. We may, therefore, define a molecule in the following way—

A molecule is the smallest particle of any kind of matter, element or compound, which can exist in the free state and possesses all the properties of that kind of matter.

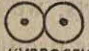
The concept of atom has been found in the Dalton's atomic theory. But it was Avogadro who gave the idea of existence of molecules. This will be considered in the next chapter. A molecule of an element contains like atoms only, whereas a molecule of a compound is made up of atoms of two or more different elements. In case of an element, a molecule may contain one atom, but a molecule of a compound can never contain less than two atoms which again should be different. During a chemical change, molecules of reacting substances first separate into atoms which then combine to form new molecules of the product. Atoms remain unaltered in all chemical changes.

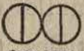
A pictorial representation of atoms and molecules are given below :—

The atom of the different elements may be represented as :—



The molecules of different compounds may then be represented as follows :—


HYDROGEN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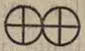
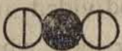
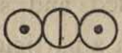
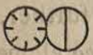
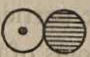

NITROGEN

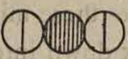
CARBON

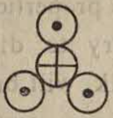

CARBONDIOXIDE

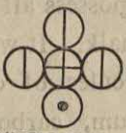

WATER


MERCURIC OXIDE


HYDROCHLORIC ACID


SULPHUR DIOXIDE


AMMONIA


NITRIC ACID

Inter molecular space—Matter consists of aggregation of large number of molecules. However, it is not continuous, but discrete. Hence there exist certain inter spaces between these molecules—this is called inter molecular space.

When a solid, like sugar, is dissolved in water, there is no appreciable increase in the volume of the solution. This is explained by the fact that sugar molecules enter into the inter molecular spaces of water. Similarly, the fact that the volume of a gas contracts on the application of pressure is also explained by supposing that there are spaces between the molecules.

Inter molecular force—The molecules, which constitute matter, are not statoinary. They always execute, rapid motion due to which the molecules tend to fly away from one another. However, the molecules of a body are held together by means of force called intermolecular force of attraction. This force is least in the gas phase and highest in the solid state.

The distinction between the three states of matter in the light of intermolecular forces has alreday been discussed in chapter I.

Under high pressure and low temperature, the intermolecular space decreases and so the intermolecular force of attraction increases. As a result the gas is transformed to liquid and gradually to solid under such conditions.

The building units of matter, i.e., the atoms and molecules are extremely minute particles, They cannot be seen even with powerful microscopes—only they are visualised in our imagination. Though some recent experimental developments help us to demonstrate the existence of these minute particles, the atoms and molecules possess extremely small weights as well as occupy infinitesimally small volume. Hydrogen and Uranium are the lightest and heaviest elements found in nature. The weights of their atoms are—

The weight of hydrogen atom $= 1{\cdot}66 \times 10^{-24}$ gms.

The weight of uranium atom $= 3{\cdot}95 \times 10^{-22}$ gms.

Similarly the weights of the molecules of differnt substances are also very small. Thus—

A molecule of oxygen weighs $5{\cdot}3 \times 10^{-23}$ gms.

A molecule of sugar weighs $5{\cdot}67 \times 10^{-22}$ gms.

The volumes of the atoms and molecules are also negligibly small. Take for example hydrogen—the diameter of its atoms are found to be $2{\cdot}4 \times 10^{-8}$ cm. or $2{\cdot}4\ A^{\circ}$ ($1A^{\circ} = 10^{-8}$ cm.). Therefore the volume of hydrogen atom comes to be equal to $13{\cdot}8 \times 10^{-24}$ cubic centimeter.

3-6. **Atomic weight :** The absolute weight of the atom of an element is too small to be determined by direct weighing. It is also difficult to use such small fractional values in all chemical calculations. However, such weights can be easily found out relative to the weight of the atoms of some standard element which has been assigned a definite value. This relative weight of the atom of an element is referred to as its atomic weight. It tells us how many times an atom of an element is heavier or lighter than one atom of another element chosen as standard. Hence,

$$\text{Atomic weight} = \frac{\text{weight of an atom of the element}}{\text{weight of an atom of the standred element}}.$$

Therefore, the atomic weight has no unit, it is merely a number and does not indicate the actual weight of an atom of the element.

At one time the weight of the hydrogen atom, the lightest known element, was chosen as the standard by Dalton and therefore the atomic weight of an element was expressed in terms of a scale on which the hydrogen atom has a weight of 1. Hence,

$$\text{Atomic weight} = \frac{\text{weight of an atom of the element}}{\text{weight of one atom of hydrogen}}.$$

Thus, the atomic weight of sodium is 23 which means that the weight of one atom of sodium is 23 times heavier than one atom of hydrogen.

Subsequently, hydrogen has been replaced by oxygen as the standard for determining atomic weights and one-sixteenth ($\frac{1}{16}$th) part of the weight of an atom of oxygen has been taken as the unit. The atomic weight, is therefore, expressed in terms of a scale on which the oxygen atom has a weight of 16.

Therefore, based on the new standard—

Atomic weight of an element

$$= \frac{\text{weight of an atom of the element}}{(\frac{1}{16}) \times \text{weight of one atom of oxygen}}$$

$$= \frac{\text{weight of one atom of the element}}{\text{weight of one atom of oxygen}} \times 16.$$

On this standard, the atomic weight of an element is the number of times one atom of it is heavier than the sixteenth part of the atom of oxygen. On the oxygen standard the atomic weights of hydrogen, chlorine, carbon, nitrogen, sodium are 1·008, 35·457, 12·01, 14·008, 22·997 respectively. Oxygen has been accepted as standard because it is easier to form compounds with oxygen than with hydrogen and the values of the atomic weights of most of the elements calcultated on this standard come very near to whole numbers.

Since 1960, carbon has been adopted as standard in place of oxygen for determining atomic weights and one-twelfth part of the weight of an atom of carbon-12 isotope has been taken as the unit. The atomic weight is now expressed in terms of a scale on which the carbon atom has a weight of 12. Hence, according to the modern standard, the expression of atomic weight is—

$$\text{Atomic weight} = \frac{\text{weight of an atom of the element}}{(\frac{1}{12}) \times \text{weight of one atom of carbon}}.$$

The selection of carbon-12 isotope as standard is due to the fact that ordinary oxygen consists of a mixture of three isotopes having atomic weights 16, 17 and 18 on the oxygen scale. The oxygen 16 standard then represent only an average weight of the mixture of these natural isotopes and the atomic weight of any element would depend on the isotopic composition of oxygen employed as the standard. Hence corbon-12 isotope has been favoured as the present standard. However, this does not affect much the atomic weight values of different elements calculated on the oxygen standard.

Due to the existence of isotopes, the atomic weight of an element shows the average weight of an atom of the element relative to the weight of the carbon atom taken as 12. On this scale the atomic weight of chlorine is 35·46. This indicates the average relative weight of an atom of chlorine as ordinary chlorine contains two types of isotopes having atomic weights 35 and 37 present in the ratio of 3 : 1. On carbon scale, the atomic weight of hydrogen has come out to be 1·0079. For all ordinary purposes this is taken as 1 and the following atomic weight values for some common elements are used for simplicity in chemical calculations—

$H = 1$, $Cl = 35{\cdot}5$, $N = 14$, $O = 16$, $C = 12$

$S = 32$, $Na = 23$, $K = 39{\cdot}1$ $Ca = 40$, $Al = 27$, $Fe = 55{\cdot}8$.

Atomic mass unit (a. m. u.) : The atomic weight expresses the relative weight only. Now a days, atomic mass unit (a. m. u.) has been introduced to calculate the mass of a single atom of the element. The carbon-12 isotope has been assigned a mass of exactly 12 atomic mass unit. Thus

$$1 \text{ atomic mass unit (a.m.u.)} = \frac{\text{mass of a carbon-12 atom}}{12}$$

$$= \frac{1{\cdot}9923 \times 10^{-22}}{12} \text{gm.}$$

$$= 1{\cdot}6603 \times 10^{-24} \text{gm.}$$

(Mass of a carbon-12 atom was found to be $1{\cdot}9923 \times 10^{-22}$gm. The calculation will be shown in the next chapter)

Atomic weight of oxygen is 16.

∴ Mass of one oxygen atom = 16 a.m.u.

$$= 16 \times 1{\cdot}6603 \times 10^{-24} \text{gm.}$$

$$= 2{\cdot}66 \times 10^{-23} \text{gm.}$$

Mass of one nitrogen atom $=14$ a.m.u. $=14\times1{\cdot}6603\times10^{-24}$gm.
$=2{\cdot}324\times10^{-23}$gm.

3-7. Gram atomic weight or gram atom :

We have seen that atomic weight is a number, it has no unit. Now the quantity of an element whose weight in grams is numerically equal to its atomic weight is called the gram atomic weight or simply the gram atom of the element. That is the gram atomic weight of an element is its atomic weight expressed in gram. Thus —atomic weight of nitrogen is 14. Therefore 14 grams of nitrogen stand for one gram atom of nitrogen. Similarly 1 gram-atom of sodium = 23 gram of sodium, 1 gram-atom of carbon = 12 gram of carbon, and soon. It can be shown that one gram-atom of all elements contain equal number of atoms. That is the number of sodium atoms in 23 grams of sodium will be exactly equal to the number of carbon atoms present in 12 grams of carbon. This number is called Avogadro's number. (See Chapter Four)

Exercises—3

1. State the fundamental postulates of Dalton's Atomic theory and indicate its utility.

2. What are the limitations of Dalton's atomic theory ? Describe briefly what modifications are attached to Dalton's original theory as a result of more modern knowledge of atomic structure.

3. Show how the different laws of stoichiometry can be deduced from Dalton's atomic theory.

4. Define an 'atom' according to Dalton. How does present day atom differ from Daltonian atom ?

5. 1) Define :—

a) atomic weight, b) gram atomic weight and c) atomic mass unit.

2) What do you understand by the statement—the atomic weight of chlorine is 35·46 ?

6. What is the difference between

a) atomic weight and b) the weight of an atom ?

What is the mass of an oxygen atom ?

CHAPTER IV

AVOGADRO'S HYPOTHESIS : THE CONCEPT OF MOLECULES

In the previous chapter the concept of molecules has been considered in order to understand the constitution of matter. But the existence of such minute particles was not visualised by Dalton in his Atomic Theory, Avogadro, an Italian physicist, was the first to recognise molecules as the freely existing particles of matter and put forward his famous hypothesis in 1811. Avogadro's hypothesis has been able to solve the controversial outcome that developed while attempting to explain the law of gaseous volumes with the help of Dalton's atomic theory.

4-1. **Adoption of Avogadro's Hypothesis** : We have already mentioned the law of gaseous volumes which was formulated by Gay-Lussac soon after Dalton put forward his atomic theory. According to this law, under identical physical conditions, elements in the gaseous state unite in simple proportions by volume. A few years earlier it was also observed that all gases behave similarly with regard to change of temperature and pressure. It was at once thought that the facts found experimentally by Gay-Lussac might be explained by Dalton's atomic theory. An attempt to correlate atomic theory with law of gaseous volumes was made by Berzelius, a Sweedish chemist. He argued as follows—

(i) The Gas-Lussac's law emphasised that the elements in the gaseous state unite chemically in simple proportions by volume, and

(ii) Dalton in his atomic theory postulated that the elements react in simple proportions by atoms.

Therefore there might be some simple relationship between the number of atoms present in equal volumes of different gases under the identical physical conditions. Berzelius proposed that equal volumes of all gases under the snme conditions of temperature and pressure contain same number of atoms. The term atom included Dalton's 'compound atom'. This is known as Berzelius hypothesis which tells us that at the same temperature and pressure, a given volume, say one litre of oxygen or ammonia or carbondioxide or any other gas contain the same number of respective atoms. But this hypothesis failed to interpret the experimental results and led to a conclusion which contradicted the very basic assumption of Dalton's atomic theory i.e., the indivisibility of atom. For example —in the reaction,

hydrogen + oxygen = steam,

it was found experimentally that,

2 volumes of hydrogen combined with 1 volume of oxygen to produce 2 volumes of steam.

Let n be the number of atoms present in unit volume of each of the reacting gases and the product. Then according to Berzelius hypothesis,

$2n$ atoms of hydrogen $+ n$ atoms of oxygen $= 2n$ compound atoms of steam,

or 2 atoms of hydrogen + 1 atom of oxygen = 2 compound atoms of steam.

or 1 atom of hydrogen $+\frac{1}{2}$ atom of oxygen = 1 compound atom of steam.

Thus, in order to produce 1 compound atom of steam, every atom of oxygen has to be divided into two portions, This is contrary to Dalton's atomic theory which assumes that atoms are the smallest conceivable particles which cannot be divded in chemical reactions. The same difficulty arises with other gaseous reactions. Berzelius hypothesis thus failed to correlate the law of gaseous volumes and the atomic theory—and was ultimately rejected.

This difficulty was overcome by Avogadro who enunciated his hypothesis in a very simple way, to explain Gas-Lussae's law without contradicting Dalton's fundamental postulate.

In order to overcome the difficulty, Avogadro for the first time differentiated between the elementary atoms and the ultimate particles of a gas. He supposed that the physical unit of a gas is not the single atom but a cluster of a small number of atoms, the number for many elementary gases is two. These clusters of atoms he called molecules and thus Avogadro recognised two kinds of ultimate paricles of matter, an atom and a molecule.

(i) an atom is the smallest indivisible particle of an element which takes part in a chemical change but may not exist in the free state.

(ii) a molecule is the smallest particle of substance (element or compound) which has free or independent existence retaining all the properties of the substance.

So, it is evident from the concept of molecules that a gas always contains very large number of such molecules and Avogadro assumed that there must be some simple relationship between the number of molecules, instead of atoms, present in equal volumes of different gases under identical physical conditions. This idea led Avogadro to enunciate his famous hypothesis which states as follows—

Avogadro's Hypothesis : *Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.*

This means that at a fixed temperature and pressure, if a vessel with a definite volume, say 1 liter, is filled up successively with different gases like hydrogen, oxygen, carbondioxide or ammonia, either elementary or compound, the vessel will contain same number of molecules (not the atoms) in all cases.

Avogadro's hypothesis cannot be experimentally verified as the molecules in a volume cannot be counted. However, the hypothesis conforms to experimental tests of deductions made from it and that is why it is now regarded as a law.

Avogadro's hypothesis successfully accounts for the volume relations of gases taking part in chemical reactions and thus removes the drawbacks of the Berzelius hypothesis. The follwing reaction may be considered as an example :

The reaction, hydrogen + chlorine yield hydrogen chloride.

Exerimentally, it is found that,

1 volume hydrogen + 1 volume chlorine yield 2 volumes of hydrogen chloride.

Let n be the number of molecules present in 1 volume of hydrogen, then by Avogadro's hypothesis ;

n molecules of hydrogen + n molecules of chlorine yield $2n$ molecules of hydrogen chloride,

or, 1 molecule of hydrogen + 1 molecule of chlorine yield 2 molecules of hydrogen chloride.

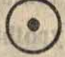
2 molecules of hydrogen chloride have been produced from 1 molecule hydrogen. Therefore, in its formation, the hydrogen molecule has been divided into two equal parts, that is it must contain even number of hydrogen atoms. On similar grounds, the molecule of chlorine must contain an even number of atoms. It will be shown later that the number is two in both cases. The reaction can therefore be expressed by the equation

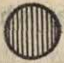
$$\underset{\text{1 molecule}}{HH} + \underset{\text{1 molecule}}{Cl\,Cl} = \underset{\text{2 molecules.}}{HCl + HCl}$$

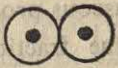
The molecules of hydrogen and chlorine have been split up into their constituent atoms during chemical change and the atoms have re-associated to form the new molecules of hydrogen chloride, but no atom has been subdivided. This, in no way, goes against Dalton's atomic theory.

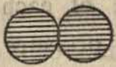
The following pictorial diagrams would clearly show how both Avogadro's Hypothesis and Gay Lussac's law are reconciled.

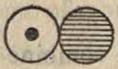
Let each rectangular vessel contain equal volumes of gases, they must also contain same number of molecules. Let us consider

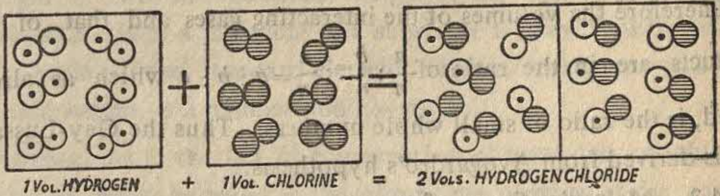
1 atom of hydrogen is represented by 

1 atom of chlorine 

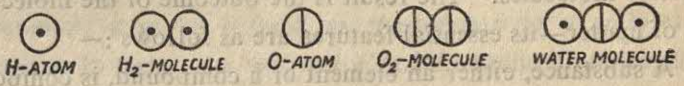
1 molecule of hydrogen 

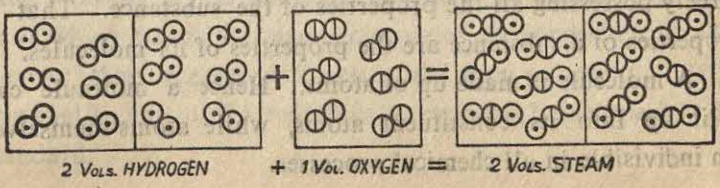
1 molecule of chlorine  and

1 molecule of hydrogen chloride by  then



Similarly, the formation of steam from hydrogen and oxygen can be expressed by the follawing diagram :





In gaseous reactions, the total volume of the reacting gases may not be equal to those of the products and as such the total number of molecules before and after the reaction may differ. But the total number of atoms remain unaltered in chemical changes.

4 2. Avogadro's Hypothesis and Gay-Lussac's Law—

The Gay-Lussac's law of gasseous volumes can be deduced from Avogadro's Hypothesis if we consider that when molecules react, they do so by simple whole numbers.

Let '*a*' molecules of gas A react with '*b*' molecules of gas B and form '*c*' molecules of the gaseous product C—we know *a*, *b*, *c*, are simple whole numbers as the fraction of molecules connot exist in the free state. Let us further suppose on the basis of Avogadro's hypothesis that 1 cc. of each gas under the same conditions of temperature and pressure contains *n* molecules. Therefore—

$\frac{a}{n}$ cc. of the gas A combine with $\frac{b}{n}$ cc. of the gas B to produce $\frac{c}{n}$ cc. of the gaseous product C.

Therefore the volumes of the interacting gases and that of the products are in the ratio of $\frac{a}{n} : \frac{b}{n} : \frac{c}{n} = a : b : c$ which as alread stated, is the ratio of small whole numbers. Thus the Gay-Lussac's law is derived from Avogardro's hypothesis.

4.3. Molecular theory of matter.—

With the adoption of Avogadro's hypothesis, the basic concepts of Dalton's atomic theory have been modified in the light of the existence of molecules. The result is the outcome of the molecular theory of matter—its essential features are as follows :—

(1) A substance, either an element or a compound, is composed of large number of minute particles, called molecules, which can exist freely possessing all the properties of the substance. That is the properties of a substance are the properties of its molecules.

(2) A molecule is made up of atoms. Hence a molecule can be split up into its constituent atoms, while atoms themselves remain indivisible in all chemical processes.

(3) A molecule of an element consists of identical atoms, while the atoms comprising the molecule of a compound are different.

(4) Atoms take part in chemical reactions while molecules do not. Hence during chemical change molecules of the reacting substances first separate into atoms (except where molecules are mon-atomic) which then combine in simple ratio to produce molecules of new substances.

4-4. Molecular weight :—Just like atom, the molecules of a substance are extremely small and possess negligible weight. The actual weight of a molecule of oxygen and that of a molecule of sugar have been found to be $5{\cdot}3 \times 10^{-23}$ grams and $6{\cdot}67 \times 10^{-22}$ grams respectively. Such small weights cannot be measured by direct weighing. However, such weights can be easily found out relative to the weight of the atom of some standard element. This relative weight of the molecule of a substance, element or compound, is referred to be its molecular weight. The molecular weight is then not the actual weight of the molecule. It tells us how many times a molecule of a substance is heavier or lighter than one atom of the standard element. Hence molecuar weight, like, atomic weight, is a number and has no unit.

According to the law of conservation of mass, the weight of a molecule must be equal to the sum of the weights of the atoms it contains, and it is, therefore convenient to express the molecular weight on the same scale as atomic weight.

Hence, the molecular weight of a substance, element or compound, may be defined as the weights of a molecule of the substance in terms of a scale on which the atom of hydrogen has a weight of 1·008 unit or the atom of oxygen has a weight of 16·00 unit. On the oxygen scale, the molecular weight of carbondioxide is 44 which means that one molecule of corbondixide is 44 times heavier than one-sixteenth part of the atom of oxygen. At present one-twelfth part of the weight of a carbon-12 isotope is taken as standard.

The molecular weight has thus been expressed as follows on different scales :—

$$\text{Molecular weight} = \frac{\text{weight of a molecule of the substance}}{\text{weight of an atom of hydrogen}^{*}}$$

$$= \frac{\text{weight of a molecule of the substance}}{(\frac{1}{16}) \times \text{weight of one atom of oxygen}}$$

$$= \frac{\text{weight of a molecule of the substance}}{(\frac{1}{12}) \times \text{weight of one atom of carbon}}$$

(* For all practical purposes, the atomic weight of hydrogen may be taken to be 1.)

Since both the molecular weight and the atomic weight are expressed on the same scale, the molecular weight of a substance can be easily calculated by adding together the atomic weights of all the constituent elements after having multiplied each atomic weight by the number of atoms of the element present in the molecule of the substance. Such calculation is possible provided the molecular formula of the substance is known :—

As for example—

Snbstance	**Molecular formula**	**Molecular weight**
Hydrogen	H_2 (diatomic molecule)	$2 \times 1 = 2$ (more correctly $2 \times 1{\cdot}008 = 2{\cdot}016$)
Water	H_2O	$2 \times 1{\cdot}008 + 16 = 18{\cdot}016$
Calcium Carbonate	$CaCO_3$	$1 \times 40 + 1 \times 12 + 3 \times 16 = 100.$

(Where 40, 12 and 16 are atomic wts. of Calaium, Carbon and Oxygen respectively)

4.5. Gram-molecular weight of a substance

The molecular weight of a substance expressed in grams is called the 'gram-molecule or gm-molecular weight.

(i) The molecular weight of glucose is 180

Hence one gm-molecule of glucose = 180 gm. of glucose

So, half of a gm.-molecule of glucose would be $\frac{1}{2} \times 180 = 90$ gm. of glucose.

(ii) The molecular weight of urea is 60

Hence 1 gm.-molecule of urea $=60$ gm. of urea.

(iii) The molecular weight of sulphuric acid $=98$

Hence 1 gm.-molecule of sulphuric acid $=98$ gms of sulphuric acid.

or, 0·1 gm.-molecule of sulphuric acid $=9{\cdot}8$ gms of sulphuric acid.

4-6. Formula weight :—

The use of the term molecular weight is not strictly acceptable in all cases. It is now known that there are substances, which actually do not exist in the molecular form. Salts like sodium chloride exist even in the solid state as ions (Na^+ Cl^-). It becomes meaningless to speak of sodium chloride molecules.

Again, from analysis of zinc sulphide we know the ratio of Zn : S in this compound is 1 : 1. But the actual molecule may be Zn_2S_2, Zn_xS_x (x being an integer) consistent with emperical ratio. It is customary and convenient to use the simplest formula. Hence, it would be better to use the term "formula weight" for the simplest formula of the substance, in place of molecular weight to avoid the uncertainty of the actual molecular composition.

The "formula weight" expressed in grams is called "gram-formula weight" or "gram-formula." The gram formula of sodium chloride is 58·5 gms and of zinc sulphide 97·3 gms.

4-7. Application of Avogadro's Hypothesis :—

Avogadro's Hypothesis is a brilliant contribution towards the development of Science of chemistry. But it took about fifty years after its adoption to assess its real worth. In 1858 Cannizzaro convinced the leading chemists of his time about the correctness of the hypothesis, which was then universally accepted. Avogadro's Hypothesis is perfectly general in its application. The hypothesis not only distinguished for the first time between atoms and molecules and explained clearly the law of gaseous volumes, it also led to the following important deductions and applications :—

(1) The molecules of elementary gases like hydrogen, chlorine, oxygen etc. are di-atomic.

(2) The molecular weight of any gaseous substance (or vapour) is twice its vapour density.

(3) The gram molecular volume of all gases is the same under like conditions of temperature and pressure and is 22.4 litres at N.T.P.

(4) It provides a method of determining the molecular formula of a gaseous substance from its volumetric composition, and also,

(5) It provides a method to determine the atomic weight of elements.

(1) To deduce that the molecules of elementary gases are diatomic, i.e., their atomicity is two.

We know from experiments, that—

1 volume of hydrogen + 1 volume of chlorine = 2 volumes of hydrogen chloride.

Let us assume that 1 volume to hydrogen gas contains n number of molecules, then by Avogadro's hypothesis, 1 volume of chlorine and 2 volumes of hydrogen chloride must contain n and $2n$ number of molecules respectively, at the same temperature and pressure.

That is,

n molecules of hydrogen + n molecules of chlorine = $2n$ molecules of hydrogen chloride.

or, 1 molecule of hydrogen + 1 molecule of chlorine = 2 molecules of hydrogen chloride.

Since hydrogen chloride is a compound of hydrogen and chlorine, each of its molecule must contain at least 1 hydrogen atom and 1 chlorine atom. Therefore, 2 molecules of hydrogen chloride must contain at least 2 hydrogen atoms and 2 chlorine atoms coming from 1 molecule of each of the gaseous elements. Hence a molecule of hydrogen and chlorine must contain at least 2 atoms. The fact that a hydrogen molecule contains two and only two atoms can be demonstrated as follows :—

(a) Acids are compounds containing replaceable hydrogen atoms which are replaced by metals to produce salts. The number of sodium salts that an acid can yield correspond to the number of replaceable hydrogen atoms in 1 molecule of the acid. Thus sulphuric acid gives two sodium salts, $NaHSO_4$ and Na_2SO_4, the molecule of the acid therefore contains two hydrogen atoms, being replaced in two stages. Now hydrochloric acid yields only one sodium salt which indicates that one molecule of hydrochloric acid contains only one atom of hydrogen. Two molecules of the acid therefore, contain two atoms of hydrogen only, which has come from one molecule of hydrogen as shown above. Therefore, hydrogen gas molecule is diatomic i.e., the atomicity of hydrogen, an elementary gas, is two.

(b) The atomicity of a gaseous substance have been proved conclusively from the value of the ratio of specific heat of the gas at constant pressurere (C_p) and at constant volume (C_v), i.e., the ratio $\frac{C_p}{C_v} = \gamma$. The value of γ, which can be obtained from experiments, depends on the number of atoms present in the molecule of the gas. Thus, it is found that $\gamma = 1{\cdot}66$ if the gas is monatomic, $\gamma = 1{\cdot}40$ if it is diatomic and so on. In case of hydrogen, the value of γ has been found to be $1{\cdot}41$, hence, hydrogen is diatomic.

Similarly, it can be shown that the atomicity of oxygen is two from the study of the following reaction :—

2 volums of hydrogen + 1 volume of oxygen = 2 volumes of steam.

Let n be the number of molecules in 1 volume of hydrogen, then by the Avogadro's Hypothesis,—

$2n$ molecules of hydrogen + n molecules of oxygen = $2n$ molecules of steam.

or 2 molecules of hydrogen + 1 molecule of oxygen = 2 molecules of steam.

or, 1 molecule of hydrogen + $\frac{1}{2}$ molecule of oxygen = 1 molecule of steam.

Hence, 1 molecule of steam, being a compound of hydrogen and oxygen, must contain at least one atom of oxygen as atom is indivisible, which must come from $\frac{1}{2}$ molecule of oxygen. Therefore, like hydrogen, oxygen molecule also contain at least two atoms. The value of γ, i.e., $\frac{C_p}{C_v}$ is found to be 1·42, so oxygen gas is also diatomic.

Thus the molecules of almost all the elementary gases consist of two atoms. However, there are some exceptions ; the gases like Helium, Neon, Argon etc. which are inert are monatomic. Their γ-values are 1·66.

(2) The molecular weight of any gas or vapour is twice its vapour (relative) density.

The vapour density of a gaseous substance or vapour is the ratio of the weight of a given volume of the gas or vapour to the weight of an equal volume of hydrogen under the same conditions of temperature and pressure. So the vapour density of a gas expresses how many times the gas is heavier relative to hydrogen under identical physical conditions.

The vapour density of Sulpher dioxide is 32. It means V cc of SO_2 is 32 times heavier that V cc, of hydrogen under the same conditions.

Now, by definition,

the vapour density of a gaseous substance or vapour,

$$D=\frac{\text{weight of } x \text{ c.c. of the gas or vapour}}{\text{weight of } x \text{ c.c. of hydrogen}}$$

(measured under the like conditions of temperature and pressure).

Now, according to Avogadro's Hypothesis, equal volumes of the gas and hydrogen contain same number of molecules,) say n. Hence,

$$D=\frac{\text{weight of } n \text{ molecules of gas or vapour}}{\text{weight of } n \text{ molecules of hydrogen}}$$

$$=\frac{\text{weight of 1 molecule of gas or vapour}}{\text{weight of 1 molecule of hydrogen}}$$

$$=\frac{\text{weight of 1 molecule of gas or vapour}}{\text{weight of 2 atoms of hydrogen}}$$

(∵ hydrogen gas is diatomic)

$$=\frac{\text{weight of 1 molecule of gas or vapour}}{2\times\text{weight of 1 atom of hydrogen}}.$$

$$\text{or } 2\times D=\frac{\text{weight of 1 molecule of the gas or vapour}}{\text{weight of 1 atom of hydrogen}}.$$

= Molecular weight of the gas or vapour. (M)

(assuming atomic weight of hydrogen = 1)

Hence molecular weight of the gas or vapour

= 2 × its vapour density.

i.e., $M = 2\times D$.

Actually the atomic weight of hydrogen is 1·008 and molecular weight is 2·016, when $O = 16$ is taken to be the standard. In that case.

Molecular weight = vapour density × 2·016.

Illustrations :—The vapour density of Carbondioxide gas is found to be 22, hence its molecular weight is 44. Similarly, the vapour density of steam is 9, therefore, its molecular weight is 18.

(3) The gram molecular volume of all gases is the same under like conditions of temperature and pressure and is 22·4 litres at N.T.P.

The gram molecular volume or simply molar volume of a substance is defined as the volume occupied by one gram-mole (the molecular weight expressed in gram) of the substance.

Now let, M be the molecular weight of a substance, and ω be the actual weight of 1 hydrogen atom in gm.

Therefore, the actual weight of one molecule of the substance $= M\times\omega$ gms.

The gram molecular weight of the substance $= M$ gms.

Hence, the number of molecules present in 1 gm. molecular weight of the substance,

$$=\frac{\text{weight of 1 gm. molecule of the substance}}{\text{weight of 1 molucle of the substance}}$$

$$=\frac{M\text{ gm.}}{M\omega\text{ gm.}}=\frac{1}{\omega}.$$

Since ω, the actual weight of one hydrogen atom, is fixed, the number of molecules in 1 gm. molecule of any substance, which is equal to $\frac{1}{\omega}$ is also constant·

Take for example—the gas ammonia has a vapour density $= 8{\cdot}5$. Therefore, its molecular weight $= 8{\cdot}5 \times 2 = 17$. (by Avogadro's hypothesis).

If ω be the actual weight of one hydrogen atom, then the weight of 1 molecule of ammonia $= 17\omega$ gms.

Now, 1 gm.-molecule of ammonia $= 17$ gms.

Therefore, in 1 gm.-molecule of ammonia, i.e., in 17 gms. of ammonia, the number of molecules, $= \frac{17 \text{ gm.}}{17\omega \text{ gm}\cdot} = \frac{1}{\omega}$.

Hence, it is found that the number of molecules present in 1 gm.-molecule of any substance is the same and is equal to $\frac{1}{\omega}$. This number, i.e., the number of molecules present in one gram-molecule of any substance is called Avogadro's number. Its value is $6{\cdot}02 \times 10^{23}$. Now, from Avogadro's Hypothesis, we can conclude that equal number of molecules of a gas or vapour must have equal volumes at the same temperature and pressure. That is the volume occupied by 1 gm.-mole of any gas or vopour i.e., the gram molecular volume, must be the same at the same temperature and pressure.

Let us now find out the value of molar volume (i. e. gram-molecular volume) of any gas at N.T.P., where N.T.P. stands for normal temperature and pressure i.e., at 0°C and 1 atmospheric pressure.

By definition of vapour density of a gas, D, we have.

$$D = \frac{\text{weight of 1 litre of the gas at N.T.P.}}{\text{weight of 1 litre of Hydrogen at N.T.P.}}$$

Experimentally it is found that 1 litre of hydrogen at N.T.P. weighs ·09 gm. (appr.)

$$\therefore \quad D = \frac{\text{weight of 1 litre of the gas (or vapour) at N.T.P.}}{\cdot 09}$$

$\therefore$ wt. of 1 litre of any gas at NTP $= (\cdot 09 \times D)$ gms.

$$= \left(\cdot 09 \times \frac{M}{2\cdot 016}\right) \text{ gms (from Avogadro's hypothesis).}$$

Where $M =$ mol. wt. of the gas or vap.

i.e. at N.T.P. $\frac{\cdot 09 \times M}{2\cdot 016}$ gms of any gas or vapour occupy a volume of 1 litre.

$\therefore$ M gms of the gas or vapour, i.e., 1 gram-molecule of any gas or vapour occupy $\frac{2\cdot 016}{\cdot 09}$ litres$\approx$22·4 litres.

That is the gram-molecular volume or molar volume of all gases or vapours at N.T P. is 22·4 litres.

On the basis of this deduction, the molecular weight of a substance can be defined in the following way :—

The molecular weight of a substance is a number, which when expressed in grams would be equal to the weight of 22·4 litres of the substance in the gaseous or vapours state at N.T.P.

As for example, at N.T.P. the weight of 22·4 litres of sulpherdioxide gas = 64 grams. Therefore, the gram-molecule or gram-mole of the gas is 64 grams, hence the molecular weight of sulphur-di-oxide is 64.

(4) Determination of the molecular formula of a gaseous substance from its volumetric composition.

By the application of Avogadro's Hypothesis, it is possible to determine the molecular formula of a gaseous compound from its volumetric composition and density. Let us take the following illustrations :—

a) Molecular formula of Ammonia :

It has been found experimentally that 1 volume of nitrogen + 3 volumes of hydrogen = 2 volumes of ammonia. Let n be the number of molecules in 1 volume of nitrogen. then by Avogadro's hypothesis,

n moleculs of nitrogen $+ 3n$ molecules of hydrogen
$= 2n$ moleculs of Ammonia

Or, 1 molecule of nitrogen $+ 3$ molecules of hydrogen
$= 2$ moleculs of ammonia,

Or, $\frac{1}{2}$ molecule of nitrogen $+ \frac{3}{2}$ molecules of hydrogen
$= 1$ molecule of ammonia.

By Avogadro's hypothesis, both nitrogen and hydrogen are diatomic, hence,

1 atom of nitrogen $+ 3$ atom of hydrogen
$= 1$ molecule of ammonia.

Therefore the proportion of the atoms of nitrogen and hydrogen in ammonia molecule is $1 : 3$. Hence its simplest formula is NH_3 and the moleculer formula is $(NH_3)_x$, where x is a small integer.

Now the vapour density of ammonia gas has been found to be 8·5 $\therefore$ its molecular weight, according to Avogadro's hypothesis is $8{\cdot}5 \times 2 = 17$.

$\therefore \quad (14+3)x = 17 \qquad \therefore \quad x = 1.$

Hence the molecular formula of ammonia is NH_3.

b) Molecular formula of nitric oxide :

By actul experiment we find that nitric oxide contains half its volume of nitrogen. Hence 1 volume of nitric oxide contains $\frac{1}{2}$ vol. of nitrogen. Let n be the number of molecules present in 1 volume of nitric oxide. Then from Avogadro's hypothesis.

n molecules of nitric oxide contains $\dfrac{n}{2}$ molecules of nitrogen

Or, 1 molecule of nitric oxide contain $\frac{1}{2}$ molecule of nitrogen

Or, 1 molecule of nitric oxide contain 1 atom of nitrogen
($\because$ nitrogen molecule is diatomic).

Hence its simplest formula is NO_x where x is a small whole number.

Now vapour density of nitric oxide has been found experimentally to be 15. Therefore, its molecular weight, according to Avogadro's hypothsis, is $15 \times 2 = 30$.

That is $14 + 16x = 30 \qquad \therefore \quad x = 1.$

Hence the molecular formula of nitric oxide is NO.

(5) Ditermination of atomic weight of an element :—

(*a*) **By Cannizzaro's method** :—

Cannizzaro, in 1858, proposed a method of determining the atomic weight of elements by utilising Avogadro's hypothesis and the basic concept of the atomic theory. The method is based on the fact that, as the atoms are indivisible, the molecule of any compound cannot contain less than one atom of any of its constituent elements. Hence, if we analyse different compounds of a particular element, the smallest weight of this particular element present in the molecular weights of these different compounds may be taken as the atomic weight of the said element.

In order to determine the atomic waight by Cannizzaor's method, the following steps are to be followed :—

(*a*) A large number of gaseous or volatile compounds of an element, whose atomic weight is to be determined, are selected and their vapour densities are determined experimentally.

(*b*) The molecular weights of these compounds are then calculated from the relation : Molecular weight = 2 × vapour density.

(*c*) These compounds are then analysed to determine their percentage composition. From this percentage composition, the weight of the particular element present in 1 gram molecular weight of each compound Is then computed.

(*d*) The least of these weights or more correctly the highest common factor (H.C.F.) of these weights may be taken as the probable atomic weight of the said element.

The following illustration will show how the atomic weight of Carbon can be found out by this method.

Determination of atomic weight of Carbon :

Volatile compounds of carbon	Vapour density	Mol. wt.	% of carbon by wt. (gm)	wt of carbon per gram-molecule (gm)
1. Carbondioxide	22	44	27·3	$44\times{\cdot}273=12{\cdot}01\approx12$
2. Methane	8	16	75·0	$16\times{\cdot}75=12$
3. Acetylene	13	26	92·3	$26\times{\cdot}923=23{\cdot}99\approx24$
4. Carbon-monoxide	14	28	42·9	$28\times{\cdot}429=12{\cdot}01\approx12$
5. Benzene	39	78	92·3	$78\times{\cdot}923=71{\cdot}99\approx72$

Since 12 gm is the least weight of carbon found in the gram molecular weight of its different volatile compounds 12 may be taken as the probable atomic weight of carbon.

By this method the atomic weight of an element cannot be. determined aecurately and the method itself is very laborious This method is applicable if an element can form large number of volatile or gaseous compounds.

(*b*) The atomic weight of a gaseous element can be obtained, by knowing the atomicity of the element using the relation ; atomic weight = molecular weight ÷ atomicity. The method for determining the atomicity of the geseous element has already been discussed. The determination of molecular weight from the vapour density measurement will be described later. Hence the atomic weight can be determined from the above relationship.

Thus, the vapour density of cholorine is 35·5, hence its molecular weight is $35{\cdot}5\times2=71$, Therefore the atomic weight of chlorine is $71\div2=35{\cdot}5$, the atomicity being two.

4·8 Avogadro's Number :—

It has been shown earlier that the number of molecules present in 1 gram molecule of any substance are equal and definite. The same number of atoms are also present in 1 gram atomic weight of any element. This fixed number of particles, atoms or molecules, present in 1 gram atomic weight or 1 gram molecular weight is known as Avogadro's Number, generally represented by N and is found to be equal to $6{\cdot}023 \times 10^{23}$. This is really a very large number and an important constant. Thus 1 gm molecule i.e. 32 grams of oxygen or 44 grams of carbondioxide or, 71 gms of chlorine, all contain $6{\cdot}023 \times 10$ molecules of each. Similarly same number of sodium atoms are present in 1 gram atom i.e. 23 gram of metallic sodium.

4.9 Absolute weight of an atom or a molecule :—

It is evident that the absolute weight of atom in grams in just $\frac{1}{N}$ times its gram atomic weight and similarly for the weight of a molecule.

That is—

The weight of an atom of an element

$$= \frac{\text{1 gram atomic weight of the element}}{\text{Avogadro's Number}}$$

and, the weight of one molecule of a substance

$$= \frac{\text{1 gram molecular weight. of the substance}}{\text{Avogadro's Number}}$$

Thus, the wt. of 1 carbon atom $= \frac{12}{N}$ (at. wt. = 12)

$$= \frac{12}{6{\cdot}023 \times 10^{23}} = 1{\cdot}99 \times 10^{-23} \text{ gm.}$$

and, the wt. of 1 molecule of oxygen $= \frac{32}{N}$ (Mol. wt. = 32)

$$= \frac{32}{6{\cdot}023 \times 10^{23}} = 5{\cdot}81 \times 10^{-23} \text{ gm.}$$

4·10. The Mole Concept :

The word 'mole' generally stands for 1 gram molecular weight or 1 gram-mole of any substance, That is molecular weight expressed in grams.

So 1 mole of oxygen means 32 grams of oxygen ; 1 mole of carbondi-oxide means 44 grams of carbondioxide and so on. Hence, if we have *x* grams of any substance, the corresponding number of moles of the substance will be $\frac{x}{M}$, where M is the molecular weight of the substance. i.e., 4 grams of hydrogen $= \frac{4}{2} = 2$ moles of hydrogen,

Or, 42 grams of nitrogen $= \frac{42}{28} = 1{\cdot}5$ moles of nitrogen.

But we have seen that 1 gram molecular weight of all substances contain same number of molecules which is also equal to the number of atoms present in 1 gram atomic weight of all elements and this fixed number, i.e., the Avogadro's number has the value $6{\cdot}023 \times 10^{23}$. As such, the 'mole' may also represent this definite number of any type of particles. Hence more conveniently one 'mole' of a substance represents the amount of the substance which contain this Avogadro's Number of paticles. The 'mole' is then considered as the unit for counting atoms, molecules, ions, electrons and other microscopic particles. The 'mole' is a collective noun and stands for a collection of $6{\cdot}023 \times 10^{23}$ number of such particles, just like a dozen or a gross refers to a collection of twelve or twenty objects. It is better to state 'one mole hydrogen atom' or 'one mole of nitrogen molecule' instead of 'one mole of hydrogen' or 'one mole of nitrogen' to indicate the type of the particles to bs counted.

Numerical Problems :

1. How many molecules of oxygen are there in cc. of the gas at NTP ? What is the absolute weight of an oxygen atom ?

In 22400 cc. of oxygen at NTP, there are $6{\cdot}02 \times 10^{23}$ molecules of oxygen.

∴ in 1 cc. of the gas, the no. of oxygen molecules are

$$\frac{6{\cdot}02 \times 10^{23}}{22400} = 2{\cdot}687 \times 10^{19}.$$

Again, 1 gr. atom of any element contains $6{\cdot}02 \times 10^{23}$ atoms.

But 1 gr. atom of oxygen = 16 gms of oxygen.

∴ $6{\cdot}02 \times 10^{23}$ atoms of oxygen weigh 16 gms.

∴ the wt. of an oxygen atom $= \frac{16}{6{\cdot}02 \times 10^{23}} = 2{\cdot}657 \times 10^{-23}$ gms

2. Air contains 20% by volume of oxygen and 80% by volume of nitrogen. Calculate its vapour density.

1000 c.c. of air contain 200 c.c. of oxygen and 800 c.c. of nitrogen.

Now, 24000 c.c. of oxygen weigh at NTP 32 gms.

∴ 200 c.c. of oxgyen weigh at NTP $\frac{32 \times 200}{22400} = {\cdot}286$ gms.

Similarly 800 c.c. of nitrogen weigh at NTP $\frac{28 \times 800}{22400} = 1$ gms.

∴ Total wt. of 1 litre of air at NTP = 1·286 gm.

We know at NTP 1 litre of H_2 weighs ·089 gms.

So, the vapour density air $= \frac{1{\cdot}286}{{\cdot}089} = 14{\cdot}4$.

(3) Calculate the molecular weight of a gas one litre of which at N.T.P. weighs 3·17 gms.

1 litre of the gas weighs 3·17 gms.

∴ 22·4 litres of the gas weighs $3{\cdot}17 \times 22{\cdot}4 = 71$ grams.

From Avogadro's Hypothesis we know that 22·4 litres are the volume of 1 gr. molecular weight of any gas.

∴ the molecular weight of the gas is 71.

4. Which of the following possess the largest number of molecules ?

(a) 4·0 gms oxygen (b) 11·0 gms carbondioxide.

(c) 3·4 gms ammonia (d) 10·0 gms Calcium carbonate.

(a) 4 gms $O_2 = \frac{4}{32}$ gr. mole of oxygen = ·125 mole of oxygen.

(b) 11 gm $CO_2 = \frac{11}{44}$ gr. mole of CO_2 = ·25 moles of CO_2

(c) 3·4 gms $NH_3 = \frac{3{\cdot}4}{17}$ gr. mole of NH_3 = ·2 moles of NH_3

(d) 10 gm $CaCO_3 = \frac{10}{100}$ gr. mole of $CaCO_3$

= ·1 mole of $CaCO_3$

Since the no. of moles in (b) is greater than in other cases,

$\therefore$ 11 gms of CO_2 has the largest number of molecules.

5. A mixture of hydrogen and oxygen contains 20% by weight of hydrogen. What is the total mumber of molecules present per gram of the mixture ?

In 100 gms of the mixture, $H_2 = 20$ gms ; $O_2 = 80$ gms.

$\therefore$ in 1 gm of the mixture ; $H_2 = \cdot 2$ gm ; $O_2 = \cdot 8$ gms.

Now ·2 gm $H_2 = \frac{\cdot 2}{2} = \cdot 1$ mole of Hydrogen

and ·8 gm of $O_2 = \frac{\cdot 8}{32} = \cdot 025$ moles of Oxygen.

$\therefore$ the total mumber of moles in 1 gr. of the mixture $= \cdot 125$.

$\therefore$ total no. of molecules present $= \cdot 125 \times 6 \cdot 02 \times 10^{23}$

$= 7525 \times 10^{19}$

Exercise—4

1. What led to the adoption of Avogadro's Hypothesis ? State the hypothesis. Why is the hypothesis called a law ?

2. Show how Avogadros' hypothesis helps us to explain the law of gaseous volume.

3. With the help of Avogadro's hypothesis, how would you prove that

(a) both hydrogen and chlorine are diatomic.

(b) if the vapour density of a gas is 22·00, its molecular weight would be 44·00.

(c) the gram molecular volume of all gases at N.T.P. is 22·4 litres.

4. An element produces several gaseous and volatile compounds. What would be the usual procedure of determining its approximate atomic weight ?

5. 1 litre of a gaseous element reacts with 2 litres of another gaseous element to form 1 litre of a gaseous compound (all the volumes being measused at the same temp. and pressure). Both the elements are known to be diatomic. Taking the symbols for the two elements as X aud Y respectively, find the molecular formula of the compound.

6. Write notes on :—

(a) Avogadro's Number, (b) Mole concept, (c) Molecular weight, d) Molar volume, (e) Gram molecular weight.

7. (a) Prove that the number of atoms present in 1 gram atomic weight of any substance are the same as the number of molecules present in 1 gram molecular weight of any substance. What is the value of this number.

(b) What does a mole of substance signify? How many moles are there in 5·06 gms of nitrogen molecules ? (0·1807 mole)

8. (a) How many molecuales of water are present in a drop of water weighing 0·05 gm ? ($1·67 \times 10^{21}$)

(b) Prove that 1 gm. of hydrogen contains greater number of molecules than 1 gm. of carbondioxide.

(c) Are the number of molecules in one mole of a gas at 100°c and 300 mm. pressure euqal to, greater than or less than the Avogadro's Number ? (equal to N)

(d) What is the average weight of a molecule of methane ?
($2·657 \times 10^{-23}$ gm).

(e) What weight of $CaCO_3$ will contain the same number of molecules as the number of atoms in 4·0 gm of oxygen ? (25 gm $CaCO_3$)

9. Analysis of any of the gaseous compounds of phosphorus shows that 1 litre of it at N.T.P. never contains less than 1·384 gm. of the element. Again 1 litre of phosphorus vapour at NTP weighs 5·536 gm. What conclusions can be drawn regarding approximent atomic weight, molecular weight, atomicity of phosphorus from above results ?

[at wt. = 31 ; Mol. wt. = 124 ; atomicity = 4]

10. 6·84 gms of sugar (Mol. wt. 342) one dissolved in 13·5 grams of water. How many molecules are there in the solution. [$4·7 \times 10^{23}$]

11. The density of helium is o·1785 gm/litre at N.T.P. It is a monatomic gas. Find out its atomic weight [3·998]

12. (a) Prove that "one gram of nitrogen and one gram of carbon monoxide will contain very nearly the same number molecules"

(b) One litre of a gas at N.T.P. weighs 1.964 gm. What is the the molecular weight ? [43·994]

13. A cylinder contains 0·28 gm. ethylene. How many (1) moles of C_2H_4, (ii) molecule of C_2H_4. (iii) atoms of carbon and (iv) atoms of hydrogen are there in it. [(i) 0·01 mole, (ii) $6·02 \times 10^{21}$ molecules, (iii) $12·04 \times 10^{21}$ C—atoms, (iv) $24·08 \times 10^{21}$ H—atoms]

CHAPTER V

SYMBOLS, FORMULA & VALENCY

In order to describe chemical changes, it has been found convenient to write the names of the elements and compounds, which are involved in such changes, in abbreviated form. The need for using abbreviations to represent the names of substances was felt even to Alchemists, who used peculiar drawings and signs for symbolising substances known to them. The mode of symbolisation changed from time to time. The present system of using chemical symbols and formulas to represent elements and compounds was suggested by Berzelius in 1811.

5-1. **Symbol :** *A symbol is the abbreviation for the full name of an element.* The name of the elements are quickly written by their symbols. Usually the initial letter of the English name of an element in capital is used to represent that element symbolically. Thus—oxygen is represented by O, the symbol for Hydrogen is H, sulphur is represented by S, Carbon by C, Nitrogen by N, Iodine by I and so on.

If the names of two or more elements commence with the same letter, then a pair of letters are neccessary. The initial letter in capital followed by a second small letter prominantly heard in pronouncing the word, are used. Symbols of some elements of this type are given below :—

Boron	B	Nitrogen	N	Carbon	C
Beryllium	Be	Neon	Ne	Calcium	Ca
Barium	Ba	Nickel	Ni	Chromium	Cr
Bromine	Br	Niobium	Nb	Cadmium	Cd
Bismuth	Bi	Neptunium	Np	Californium	Cf

Sometimes, the symbols are divided from the Latin (or German) names of the elements. Some examples are given below :—

English name	Latin name	Symbol
Sodium	Natrium	Na
Potassium	Kalium	K
Copper	Cuprum	Cu
Silver	Argentum	Ag
Gold	Aurum	Au
Mercury	Hydrargyrum	Hg
Iron	Ferrum	Fe
Lead	Plumbum	Pb
Tin	Stannum	Sn
Tungsten	Wolfram (German name)	W

Symbols of few familiar elements are as follows :—

Aluminium	Al	Magnesium	Mg
Arsenic	As	Manganese	Mn
Barium	Ba	Nickel	Ni
Bromine	Br	Nitrogen	N
Calcium	Ca	Oxygen	O
Carbon	C	Phosphorus	P
Chlorine	Cl	Platinum	Pt
Fluorine	F	Silicon	Si
Hydrogen	H	Sulphur	S
Iodine	I	Zinc	Zn

A symbol has got both qualitative and quantitative significance. It stands normaly for the name of the element, but also denotes one atom of the element and a quantity proportional to the atomic weight of the element. Thus the symbol Cl represents (i) the name chlorine, (ii) one atom of cholorine and (iii) 35.5 parts by weight of chlorine. Similarly 2Cu represents (i) the name copper, (ii) two atoms of copper and (iii) $2 \times 63{\cdot}5 = 127{\cdot}0$ parts by weight of copper.

Formula : All kinds of matter, elements or compounds are nothing but the agglomeration of large number of molecules. *Formula (or molecular formula) is the symbollic representation of the composition of the molecule of the substance.* It is wtitten using symbols and numerals, in such a way as to indicate what kinds of atoms and how many of each are present in one molecule of the substance.

The chemical formula of an element is denoted by writing first the symbol of the element and then placing a numeral to its right and a little below it to indicate the atomicity of the molecule. The molecules of hydrogen, oxygen, nitrogen, chlorine are diatomic, hence their formulas are H_2, O_2, N_2 and Cl_2 respectively. Where molecules of elements are monatomic, their formulas will be the same as their symbols, viz. the fomulas of Neon, Argon, Zinc, Copper, mercury, sodium etc. are Ne, A, Zn, Cu, Hg, Na, respectively.

A molecule of a compound contains a fixed number of atoms of its constituent elements. The chemical formula of a compound is represented by writing side by side, symbols of its constituent elements with a numeral slightly below the right hand side of each symbol to indicate the number of atoms of each element present in molecule of the compound. Thus, each molecule of water contains two hydrogen and one oxygen atoms, hence its formula is H_2O. A molecule of nitric acid contains one hydrogen atom one nitrogen atom and three oxygen atoms, hence its formula is HNO_3. The formula of Cane Sugar is $C_{12}H_{22}O_{11}$ as the molecule of it is made up of 12 atoms of Carbon, 22 atoms of hydrogen and 11 atoms of oxygen.

Formula of a few Common Compounds are as follows :

Calcium oxide (lime)—CaO
Sodium chloride (common salt) —NaCl
Calcium Carbonate (lime stone) $CaCO_3$
Potassium iodide—KI
Hydrogen sulphide—H_2S
Ammonia—NH_3
Sodium Carbonate (Soda) —Na_2CO_3

Hydrochloric acid—HCl
Sodium hydrocloric—NaOH (causticsoda)
Zine Sulphate—$ZnSO_4$
Alcohol—C_2H_6O
Cane sugar—$C_{12}H_{22}O_{11}$
Potassium Permanganate—$KMnO_4$
Calcium Phosphate—$Ca_3 (PO_4)_2$

Like symbol, the formula also has both qualitative and quantitative significance. The formula H_2O conveys the following informations—(i) the name water, (ii) one molecule of water, iii) Composition of water, each molecule of water is Composed of 2 atoms of hydrogen and 1 atom of oxygen, and (iv) 18 parts by weight of water, which is composed 2 parts by weight of hydrogen and 16 parts by wt. of oxygen.

A number placed to the immediate left of a chemical formula indicates the number of molecules of the substance. For example, $5NH_3$ indicates 5 molecules of ammonia, $10H_2$ indicates 10 molecules of hydrogen, and so on.

As nitrogen molecule ls diatomic, N_2 represents its molecular formula, but 2N denotes two separate nitrogen atoms.

Another point is to be noted in writing molecular formulae. The formula for water is H_2O, but never written as OH_2, Similarly the formula for common salt is NaCl but not written as ClNa. The reason is that a general convention is followed in the order of placing the symbols of different elements in the formula of the compound. Usually the symbol of the more electropositive element is placed first followed by the less electropositive element. So hydrogen being electropositive and oxygen being electronegative element, the formula for water is written as H_2O. Of course, there are exceptions to it.

5-3. Valency : The chemical nature of an atom is revealed by the manner in which it combines with other atoms to form molecules. This is summed up in the term valency. Valency is broadly the property of an atom of an element which enable it to enter into chemical combination with other atoms. The concept of valency has been developed historically with the growth of chemisty. Here we shall discuss only the classical idea of valency. The modern concept of valency and nature of valency bonds will be developed at a later stage after the discussion of the atomic structure.

Chemical affinity between substances is a measure of their tendency to react. Usually substances with opposite chemical nature enter into a chemical reaction as they possess strong chemical affinity to unite readily. Thus metals or electropositive elements combine with non-metals or electronegative elements. The molecule of a compound is formed by the union of atoms of different elements in simple numerical proportions. The atoms of the various elements, however, differ in their combining capacities. By comparing the experimentally determined formulas of several compounds of the same element it has been found that the formulas are not alike. Thus in the formation of metallic chlorides, there are some cases where one metal atom combines with only one chlorine atom—$NaCl$, KCl; in others with two atoms of chlorine—$CaCl_2$, $MgCl_2$; and in case of $AlCl_3$, $AuCl_3$ one atom of Al or Au combines with three atoms of chlorine. Hence it is evident that the atoms of varions elements differ in their combining capacities. Similarly, if we consider the compounds of hydrogen with various elements viz, Hydrochloric acid HCl, Water H_2O, Ammonia NH_3 and Methane CH_4, we find that one atom of each of the elements chlorine, oxygen, nitrogen and carbon is capable of combining with 1,2,3 and 4 atoms of hydrogen respectively. This shows that atoms of different elements possess dfferent capacities for combining with hydrogen. Carbon atom has got four times the combining capacity of that of hydrogen atom, The combining capacity of the aton of an element is denoted by the term valence or valency. The atom of hydrogen has been taken as the standard for measuring the valencies of the atoms of different elements—The valency of hydrogen is taken to be equal to 1 and the valency of an element is measured by the member of hydrgen atoms which combine with or are displaced by one atom of the element. Thus valency is expresed by integral number. Hydrogen is chosen as standard because it does not combine with more than one atom of any other element (except hydrazoic acid N_3H)—this has the least combining capacity.

The valance or valency of an element is the combining capacity of the atoms of the element and is measured by the number of hydrogen *atoms which combine with or are displaced by one atom of the element.*

The examples mentioned above, therefore, tell us that chlorine oxygen, nitrogen and carbon are univalent, bivalent, trivalent and tetravalent respectively.

When an element does not directly combine with hydrogen or displaces it from a compound, its valency is determined with reference to other elements of known valency, specially chlorine or oxygen. Thus, aluminium does not combine with hydrogen, but combines with three atoms of chlorine producing $AlCl_3$, aluminium chloride, so the valency of aluminium is three, ie., trivalent. Oxygen is bivalent, and consequently when one atom of oxygen combines with one atom of another element, the latter is also bivalent, e.g., calcium is bivalent in calcium oxide, CaO.

The inert gases, He, Ar, Ne, etc. do not show any tendeny to combine with any other element. Their combining capacity i.e., valency is nil—they are zero-valent. Amongst other elements, the valency may be as high as eight. Examples :

monovalent—Na, K, Ag, Cl, Br
divalent—Ca, Mg, Zn, O, S
trivalent—Al, Fe(ic.) B, N
tetravalent—C, Si, Pb
pentavalent—P, N, As
hexavalent—Cr, S
heptavalent—Mn, octavalent—Os

Variable Valencies : The valency of an element is not a constant property. It may sometimes vary—thus elements like iron, copper, nitrogen, sulphur, gold etc. exhibit more than one type of valence. This is evident from the *Law of Multiple Proportions.* The following examples would prove it.

Element	*Valency*	*Compound*	*Formula*
Iron (Fe)	2	Ferrous chloride	$FeCl_2$
	3	Ferric chloride	$FeCl_3$
Phosphorus(P)	3	Phosphorus trichloride	PCl_3
	5	Phosphorus pentachloride	PCl_5
Nitrogen(N)	3	Ammonia	NH_3
	5	Nitrogen pentoxide	N_2O_5

The following table shows some common elements having variable valencies :

Element	Symbol	Valency
Antimony	Sb	3, 5
Bromine	Br	1, 3, 5, 7
Chlorine	Cl	1, 3, 5, 7
Copper	Cu	1, 2
Chromium	Cr	2, 3, 6
Gold	Au	1, 3
Iron	Fe	2, 3
Lead	Pb	2, 4
Manganese	Mn	2, 3, 4, 6, 7
Nitrogen	N	1, 2, 3, 4, 5
Phosphorus	P	3, 5
Sulphur	S	2, 4, 6
Tin	Sn	2, 4

The compounds in which the element exhibits the lower valencies are generally termed '-ous' while those in which the higher valencies are exhibited are known as '-ic' compounds. Thus we have,

$FeCl_2$—Ferrous chloride	Hg_2O—Mercurous oxide
$FeCl_3$—Ferric chloride	HgO—Mercuric oxide

Sometimes, when an element form several compounds due to its variable valencies, these compounds are distinguished from one another by employing a system of numerical prefixes mono,-di,-tri-, etc. Thus we have CO—carbon monoxide ; CO_2—carbon dioxide N_2O—nitrous oxide ; NO—nitric oxide ; N_2O_3—nitrogen trioxide, N_2O_4—nitrogen tetroxide ; N_2O_5—nitrogen pentoxide.

According to what is known as Abegg's rule, some of the elements show one type of valence when united with hydrogen and another type when combined with oxygen ; but the sum of these two types of valences is always 8 ; e.g.,

CH_4(4)	PH_3(3)	H_2S(2)	HCl(1)
CO_2(4)	$P\ O_5$(5)	SO_3(6)	Cl_2O_7(7)

Radicals and their Valencies :

The valency concept pertains not only to individual atoms, but also to certain groups of atoms which enters into the composotion of chemical compounds and takes part in chemical reactions as a single integral unit. These groups of atoms which have no independent existence are called radicals. NH_4 (ammonium), OH (hydroxyl), SO_4 (Sulphate), NO_3 (nitrate), CO_3 (carbonate) etc. are some of the most common radicals. Radiclas have their individual characterisic valencies. One SO_4 radical unites with two hydrogen atoms to form a sulphuric acid molecule. Hence SO_4 radical is bivalent. Similarly the nitrate, NO_3 radical is univalent in nitric acid, HNO_3, the phosphate radical PO_4 is trivalent in phosphoric acid, H_3PO_4. $KMnO_4$ shows that the valency of permanganate radical, MnO_4 is one. The valencies of some of the radicals are given below :—

Radical	Valence	Radical	Valence
Amomnium NH_4	1	Carbonate CO_3	2
Nitrite NO_2	1	Bicarbonate HCO_3	1
Nitrate NO_3	1	Phosphate PO_4	3
Hydroxyl OH	1	Silicate SiO_3	2
Sulphite SO_3	2	Ferrocyanide $Fe(CN)_6$	4
Sulphate SO_4	2	Ferricyanide $Fe(CN)_6$	3
Bisulphite HSO_3	1	Permanganate MnO_4	1
Bisulphate HSO_4	1	Thiosulphate S_2O_3	2
Chlorate ClO_3	1	Dichromate Cr_2O_7	2

Except NH_4 which is a positive radical, the rest are negative radicals and play the part of a non-metallic element in a compound.

Positive and Negative Valences :

A distinction between positive and negative valences has been made in order to differentiate the nature of the combining properties of the elements. The metals and hydrogen have been assigned positive valence whereas all nonmetals (except hydrogen) are assigned negative valence. In compounds like some metal hydrides, hydrogen shows negative valence. Hence an element with (+) valency means that it is ellectropositive and constitutes the positive part of the compound or produces (if ionised) positive ion (cation) in solution. Similary, an element with (−) valency means that it is electronegative and form the negative component of the compound or produces (it ionised) the negative ion (anion) in solution. Thus, in $CaCl_2$, valences of calcium is +2 and that of chlorine is −1. For radicals also, there are positive and negative valences. All the radicals possess negative valencies except NH_4 radical which has been assigned positive valence. When a radical is associated with positive valency, it is known as a basic radical and that with negative velency is called an acid radical.

5-4. Formulæ from Valencies :

As a compound is electrically neutral, it should be remembered that, in a molecule, *the total number of positsve valencies is alway equal to the total number of negative valencies.* As for example ; in sodium chloride $Na^{+1}Cl^{-1}$, the positive valency is one, the negative valency is also one (The valencies are indicated above the symbols). In $\overset{+1\times3}{Na_3}\overset{-3}{PO_4}$, the total positive valency = +3, the total negative valency = −3. In $\overset{+3\times2}{Al_2}(\overset{-2\times3}{SO_4})_3$ both the positive and negative valencies are equal to six. From this concept it is easy to write the formulæ for different compounds.

Suppose n_1 atoms of A having a positive valency v_1 combine with n_2 atoms of B having a negative valency v_2 to form the compound $A_{n_1}B_{n_2}$. Then,

the total positive valency $= n_1 \times v_1$

and the total negative valency $= n_2 \times v_2$

Since, $n_1 v_1 = n_2 v_2$, we have

$\frac{n_1}{n_2} = \frac{v_2}{v_1}$ That is, number of atoms of the two partners in the molecule of a binary compound will be in the inverse ratio of their valencies.

The same principle would apply it *A*, *B* are radicals. To arrive at a formula of a compound *AB*, the following steps are to be followed.

(i) The symbols of *A* and *B* are written side by side—the metal or more positive element or radical to the left and the non-metal or less positive element or radical to thc right.

(ii) The valencies, indicated by numerals, are then put to the right (and a little below) of the symbals in inverse order, i.e., that of one to the other, to show the number of atoms of *A* and *B* present in the compound *AB*.

(iii) When a subscript '1' is needed after the symbol, it is not written. Whenever the subscripts are the same, they are omitted.

Examples : What would be the formuia for the compounds,

(a) Mercuric chloride, (b) Aluminium phosphate, (c) Potassium dichromate and (d) Magnesium nitride.

(a) The valency of Hg(ic) $= +2$; the valency of chorine $= -1$.
∴ formula of mercuric chloride is $HgCl_2$.

(b) The valency of $Al = +3$; the valency of phosphate $(PO_4) = -3$ ∴ Aluminium phosphate $= Al_3\ (PO_4)_3$ or simply $Al\ PO_4$.

(c) The valency of $K = +1$; the valency of $(Cr_2O_7) = -2$
∴ Potassium dichromate is $K_2Cr_2O_7$.

(d) The valency of $Mg = +2$; the valency of nitrogen $= -3$,
∴ Magnesium nitride is Mg_3N_2.

N. B. The formula of hydrogen peroxide is H_2O_2 and not HO, since a molecule of Hydrogen peroxide actually contains 2 atoms of H and 2 atoms of O.

This principle also enable one to find out the valency of an element from the molecular formula.

Examples :

(i) What is the valency of nitrogen in HNO_3 ? Let the valency of nitrogen be *x*. Remebering that total sum of positive and negative valencies would be Zero, we can write,

$$\begin{array}{lll} H & N & O_3 \\ +1 & +x & +(-2\times 3)=0 \end{array} \quad \text{or } x = +5$$

(ii) What are the valencies of iron in potassium ferrocyanide $K_4[Fe(CN)_6]$ and potassium ferricyanide $K_3[Fe(CN)_6]$. The valence of $(CN) = -1$.

In $K_4[Fe(CN)_6]$; $K_4 \quad Fe \quad (CN)_6$

$+1 \times 4 + x + (-1) \times 6 = 0$

$\therefore$ the valency of iron, $x = +2$.

In $K_3[Fe(CN)_6]$; $K_3 \quad Fe \quad (CN)_6$

$+1 \times 3 + y + (-1) \times 6 = 0$

or, the valency of iron $y = +3$.

There are, however, certain apparent exceptions in the application of this principle as in the case of H_2O_2, C_2H_4 etc. This will be discussed in concetion with "oxidation numbers."

5-5. Percentage Composition from formulae :

The percentage composition of a compoud states the weight of each constituent in 100 parts by weight of the substance. When the formula is given, the molecular weight of the substance is known from the atomic weights. Hence, the gm-atoms of the constituent atoms in a gm-molecule of the substance is also known. This would directly provide the percentage of the constituent elements in the compound.

Illustrations : (i) Calculate the percentage composition of anhydrous Sodium sulphate. Its molecular formula is Na_2SO_4.

The molecular weight of Na_2SO_4 is

$$2 \times 23 + 32 + 4 \times 16 = 142.$$

Hence 1 gm-mole of the anhydros salt i. e. 142 gm Na_2SO_4 contains 46 gm Na, 32 gm S and 64 gm of oxygen.

Therefore, percentage of $Na = \frac{46}{142} \times 100 = 32.40\%$

$$\text{percentage of } S = \frac{32}{142} \times 100 = 22.53\%$$

$$\text{percentage of } O_2 = \frac{64 \times 100}{142} = 45{\cdot}07\%$$

(ii) What is the percentage of water in crystals of blue vitriol, $CuSO_4, 5H_2O$? $(Cu = 63.5)$.

Mol. wt. of Blue vitriol $=63{\cdot}5+32+4\times 16+5\times 18=246.5.$

1 gm. mol of Blue vitriol has 5 gm mole of H_2O.

249.5 gm of Blue vitriol has $(5\times 18)=90$ gm H_2O.

$\therefore$ percentage of H_2O in Blue vitriol

$$=\frac{90}{249.5}\times 100=36.07\%$$

(iii) Estimate the phosphorus present in $Ca_3 (PO_4)_2$ as $P_2 O_5$ [Ca=40, P=31]. Calcium phosphate, $Ca_3 (PO_4)_2$ may be supposed to be made up as (3CaO), P_2O_5.

So 1 gm. mole contains 1 gm-mole P_2O_5.

Now mol. we. of $Ca_3 (PO_4)_2=40\times 3+31\times 2+16\times 8=310.$

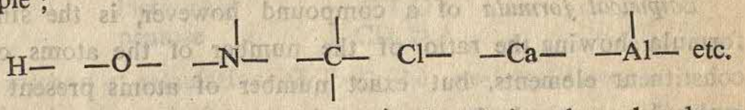
mol. wt. of $P_2O_5=31\times 2+16\times 5=142.$

310 gm of $Ca_3 (PO_4)_2$ supplies 142 gm. P_2O_5.

Hence, percentage of $P_2O_5=(142/310)\times 100=45.8\%$

5-6. Valence Bonds : Structural Formulae

To understand clearly how the valences help in uniting atoms and to have a true pricture regarding a compound, the valences of an atom are visualised and represented by attaching the necessary number of small lines or hyphens to the symbol for the element. These lines or hyphens are called "bonds" of the atoms. For example ;



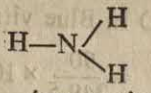
$$\mathrm{H}- \quad -\mathrm{O}- \quad -\overset{|}{\mathrm{N}}- \quad -\underset{|}{\overset{|}{\mathrm{C}}}- \quad \mathrm{Cl}- \quad -\mathrm{Ca}- \quad -\overset{|}{\mathrm{Al}}- \quad \text{etc.}$$

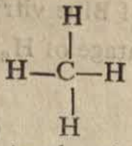
When atoms unite to form molecules, their valence-bonds are joined togather. These bonds unite in pairs, one bond of one atom can link up with only one bond of another atom and not more than one· The representation of molecules with the help of valence bonds, are called "Struetual Formulæ." From the Structual formulæ, the linking of the atoms can be understood. A pair of mutuallay satisfying bonds produce a single bond in a compound. Similarly, two pairs of bonds produce a double bond and three pairs a tripple bond.

The fundamental understanding of valence and the reason for chemical union are based on the knowledge of atomic structures, which will be considered in later chapters. The Structural formula of few compounds are show below :—

$H-Cl$
(hydrogen) chloride

$H-O-H$
(water)

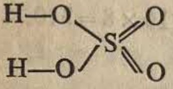

(ammonia)

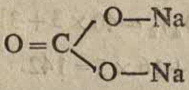

$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H$
(methane)

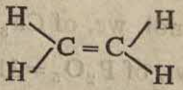
$Cl-Ca-Cl$
(celcium chloride)

$Mg=0$
(magnesium oxide)

$H-C\equiv C-H$
(acetylume)


(Sulphuric acid


(Sodium carbonate)


(ethylene)

5-7. Molecular Formula and Empirical Formula :

We have seen how the molecular formula of a compound can be determined from the knowledge of valence of constituent atoms. The "*molecular formula*" of a substance shows the actual number of atoms present in a molecule of the compound and therefore, the ratio of the number of atoms would also be known from the molecular formula.

Empirical formula of a compound however, is the simplest formula showing the ratio of the number of the atoms of the constituent elements, but exact number of atoms present in a molecule may not be known from the empirical formula.

Thus, $C_6H_{12}O_6$ is the molecular formula of glucose, which shows that one molecule of glucose contains 6 atoms of carbon, 12 atoms of hydrogen and 6 atoms of oxygen. That is the ratio of $C : H : O = 1 : 2 : 1$. The formula CH_2O has the same atomic ratio $C : H : O = 1 : 2 : 1$. It is the empirical formulæ of glucose. It has the required ratio but does not indicate the exact number of atoms present in the molecule.

Similarly, for benzene, the molecular formula is C_6H_6, but its emplrical formula is CH.

Distinctions between the Empirical formula and Molecular formula :—

(i) The empirical formula shows the ratio between the number of atoms of the elements present in one molecule of the substance, while the molecular formula shows the actual number of atoms present in one molecule.

(ii) The emperical formula can be deduced from the percentage composition (by weight) of the compound. But to determine the molecular formula, the molecular weight of the compound must be known in addition to its percentage composition.

(iii) The empirical formula is the simplest formula, but the molecular formula must be an integral multiple of the empirical formula.

(iv) It is possible that sometimes different campounds, having different molecular formula, may have the same empirical formula. For instance :

	Compound	Empirical formula	Molecular formula
1.	acetylene	CH	C_2H_2
	benzene	CH	C_6H_6
2.	glucosc	CH_2O	$C_6H_{12}O_6$
	lactic acid	CH_2O	$C_3H_6O_3$
	pentose	CH_2O	$C_5H_{10}O_5$

The method of calculations for both the empirical formula and the molecular formula from the percentage composition will be discussed in subsequent chapter.

Exercises—5

1. Define the term valency and illustrate it with suitable examples. Mention one metal and one non-metal having more than one kind of valency. Give also the formulae of their oxides and chlorides.

2. Explain clearly with examples how valences are used in writing the correct formulae of the compounds.

3. a) What are meant by positive and negative valences ?
   b) What is the valency of

(i) Phosphorus in H_3PO_4 ; (ii) Sulphur in H_2SO_4

(iii) Manganese in $KMnO_4$ and (iv) Chromium in $K_2Cr_2O_7$

[Valences of H = +1; O = —2 ; K = +1]

4. a) What information we get regarding a chmemical compound by its formula ?

(b) The formula of Phosphoric acid is H_3PO_4. If the formula of the chloride of a metal M be MCl_2, what is the formula of phosphate of this metal ?

5. (a) Estimate the percentage of

(i) calcium in $Ca(NO_3)_2$ (24·4%)

(ii) nitrogen in urea ($NH_2.CO.NH_2$) (46·66%)

(iii) lead in white lead [$2PbCO_3\ Pb(OH)_2$] (80·13%)

(iv) Chlorine in carnalite [$KCl.MgCl_2, 6H_2O$] (38·37%)

(At. Wts. H = 1, O = 16, N = 14, C = 12, Ca = 40. Pb = 207, K = 39, Mg = 24)

(b) calculate the percentage composition of the Compounds whose formulae are given below :

(i) H_2SO_4 (ii) $C_6H_{12}O_6$ (ii) $K_2Cr_2O_7$

[At. Wts : S = 32, Cr = 52]

[(i) 2·041 %H, 32·653 %S, 65·306 %O, (ii) 40 %C, 6·67 %H, 53·33 %O,

(iii) 26·58 %K, 35·45 %Cr, 38·07 %O]

6. (a) What proportion of water by weight is present in the following hydrated crystals.

(i) Barium chloride, $BaCl_2\ 2H_2O$?

(ii) Borax, $Na_2B_4O_7.\ 10H_2O$?

[At Wts : Na = 23, Ba = 137·4, B = 10·8]

[(i) 14·73%, (ii) 47.22%]

(b) What is the percentage of (i) Carbondioxide in $CaCO_3$ and

(ii) Silica in kaolin (Al_2O_3, $2SiO_2$, $2H_2O$) ?

[At. Wts : Al = 27, Si = 28, Ca = 40]

[(i) 44%, 46·51%]

7. (a) Distingnish between (i) empirical formula and

(ii) molecular formula of a compouud.

(b) What is a structural formula ? What is its importance over the molecular formula ?

8. Answer the following.—

a) The symbole Cl implies———gm and———atoms of chlorine.

b) 12 gm of carbon is one————of carbon.

c) Water contains————percent of hydrogen and————percent of oxygen by weight.

CHAPTER—VI

CHEMICAL EQUATIONS

6-1. Chemical Equations :—

Matter undergoes a chemical change through chemical reaction. In chemical change the reacting substances or reactants are transformed into new substances called products or resultants. Since every substance whether element or compound, can be represented by a symbol or formula, the chemical reaction, itself may be exprssed by an equation involving symbols and formula. The symbolic expression used to describe a chemical reaction, is termed as chemical equation.

A chemical equation, therefore, represents with the help of symbols and formulae, a chemical change that actually occurs.

To illustrate : Carbon burns in oxygen to produce corbon-dioxide. We can write,

Carbon + oxygen = Carbondioxide

or, $C + O_2 = CO_2$

Calcium Carbonate decomposes on heating into lime and Carbondioxide,

Calcium Carbonate = lime + Carbondioxide

or, $CaCO_3 = CaO + CO_2$.

Such a representation of chemical change by writing chemical equation not only saves time and space, but also has the distinct advantage of being universally understood because the expression in one language will not be intelligible to all people.

6-2. Writing a Chemical Equation :

In writing a chemical equation certain rules are to be followed which are mentioned below :—

(i) All the reactants and products must be definitely known as a chemical equation should represent only that reaction which takes place in reality.

(ii) The reactants are placed on the left hand side and are connected with plus (+) sign if there are more than one reactant.

(iii) Similarly, the products are placed on the right-hand side using plus (+) signs to connect them.

(iv) A sign of equality (=) is put between the reactants and the products which stands for the word 'to produce'.

(v) All the reactants and products are to be written by their molecular formula and not by symbols,

In the case of metals and other monatomic substances, of course, symbols and molecular formula are the same.

(vi) The equation must be a balanced one, i.e., the total number of each kind of atom on the left hand side must be equal to that on the right hand side in order to be consistent with the law of conservation of mass. To achieve this equality in the number of atoms of each element- proper coefficients for the molecules are to be used.

6.3. Balancing a chemical equation :—

(a) This is often done by *trial and error* method. Some examples are given below ;

1. Hydrogen combines with oxygen to produce water. By using the molecular formulæ, me way write,

$$H_2 + O_2 \rightarrow H_2O.$$

In this equation, total No. of oxygen atoms are unequal. Since 1 molecule of water contains 1 atom of oxygen, there must be two molecules of water to balance the number of oxygen atoms on both the sides. But in doing this 4 atoms of hydrogen will be on the right hand side. To equate the number of atoms of hydrogen on both the sides, there must be 2 molecules of hydrogen on the left hand side. Thus $2H_2 + O_2 = 2H_2O$ is the corrected balanced equation.

II. Aluminium reacts with hydrochloric acid giving off hydrogen and producing Aluminium chloride.

Writing all the substances by their molecular formulæ, we have,

$$Al + HCl \rightarrow AlCl_3 + H_2$$

In order to have the equal number of chlorine atoms on both the sides, 3 moleculs of HCl musյ be taken, which will produce $\frac{3}{2}$ molecules of H_2 to equal the number of hydrogen atoms in the two sides. Hence the equation would be

$$Al + 3HCl \rightarrow AlCl_3 + \tfrac{3}{2}H_2.$$

But fraction of molecules cannot react, so both the sides are multiplied by 2, and we have,

$$2Al + 6HCl - 2AlCl_3 + 3H_2$$

This is the correct from of the balanced equation.

III. Steam reacts with red hot iron to produce ferrosoferric oxide and hydrogen,

$$Fe + H_2O \rightarrow Fe_3O_4 + H_2 \text{ (all in molecular foruulæ)}$$

This is not a balanced one, as none of the elements except H have equal number of atoms in the two sides. To supply 3 atoms of Fe to its oxide, 3 Fe must be required and 4 atoms of O of the oxide can be obtained only from 4 molecules of water. These 4 moleculs of water would produce 4 molecules of hydrogen. So,

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

is the properly balanced equation.

In this way a regular practice by following the above steps will enable one to balance most of the chemical equations easily.

(b) *Balancing by partial equation* :

It may be difficult to balance some complicated chemical equations by trial and error method. In such cases, (i) the possible likely changes of the ingredients are considered to occur in several steps. (ii) Every step is expressed in the form of a balanced equation, called *partial equation*. (iii) the partial equation of the intermediate steps are how added up in such a way as to eliminate any intermediate species formed. (iv) if necessary, the partial equations are multiplied by suitable integers for correctly balancing the final equation.

The method is illustrated by a few examples ;

I. Copper reacts with hot and cocentrated sulphuric acid to produce sulpher dioxide, water and copper sulphate, eg.

$$Cu + H_2SO_4 \rightarrow CuSO_4 + SO_2 + H_2O.$$

Sulphuric acid is supposed to decompose on heating into Sulpher dioxide, water and oxygen. This oxygen then oxidises Cu to CuO which is then dissolues in H_2SO_4 to give $CuSO_4$ and H_2O ; thus—

$$H_2SO_4 = SO_2 + H_2O + O$$

$$Cu + O = CuO$$

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

Ading, $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$

II. An acidified solution of potassium permanganate is reduced by hydrogen peroxide to potassium sulphate, manganous sulphate, water and oxygen. That is

$$KMnO_4 + H_2SO_4 + H_2O_2 \rightarrow K_2SO_4 + MnSO_4 + H_2O + O_2$$

It is intutively suggested that $KMnO_4$ breaks up into oxygen and metallic oxides, which are dissoled by acid (H_2SO_4) to give salt and water. H_2O_2 also breaks up releasing oxygen. The steps are :

$$2KMnO_4 = K_2O + 2MnO + 5O$$

$$K_2O + H_2SO_4 = K_2SO_4 + H_2O$$

$$2MnO + 2H_2SO_4 = 2MnSO_4 + 2H_2O$$

$$5H_2O_2 = 5H_2O + 5O$$

$$5O + 5O = 5O_2$$

Summing up ; $2KMnO_4 + 3H_2SO_4 + 5H_2O_2$
$= K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

III. Potassium iodide reacts with hot and concentrated Sulphuric acid, evoling violet vapours of iodine and produces potassium bisulphate, water and sulphur dioxide. That is,

$$KI + H_2SO_4 \rightarrow KHSO_4 + H_2O + SO_2 + 1_2$$

The equation may be built up as follows ;

$$2KI + 2H_2SO_4 = 2KHSO_4 + 2H1$$

$$H_2SO_4 = H_2O + SO_2 + O$$

$$2HI + O = H_2O + 1_2$$

Adding ; $2KI + 3H_2SO_4 = 2KHSO_4 + 1_2 + SO_2 + 2H_2O$

This is the properly balanced equation the intermediates HI and O are eliminated.

(c) **Algebraic method :** By using algebraic technique, the complicated chemical equations can be balanced quite easily. This method can be well understood from the following illustrations :

I. In the reaction between copper and moderately strong nitric acid, the unbalanced equation is

$$Cu+HNO_3 \rightarrow Cu\ (NO_3)_2+NO+H_2O.$$

To balance it, suppose *a, b, c, d, e* are the number of molecules of the different substances, such as ; $a\ Cu+b\ HNO_3=c\ Cu\ (NO_3)_2+d\ NO+e\ H_2O$.

The problem is to evaluate the coefficients *a, b, c, d, e* to make the equation balanced.

To equalise for

(i) atoms of Cu ; $a=c$
(ii) atoms of H ; $b=2e$
(iii) atoms of N ; $b=2c+d$
(iv) atoms of O ; $6b=6c+d+e$

Now, let us arbitrarily put $b=1$, then from (ii) $e=\frac{1}{2}$ and from (iii) and (iv), $d=\frac{1}{4}$, from (i) and (iii), $a=c=\frac{3}{8}$. So,

$$\tfrac{3}{8}Cu+HNO_3=\tfrac{3}{8}Cu\ (NO_3)_2+\tfrac{1}{4}NO+\tfrac{1}{2}H_2O$$

Since fraction of moleculs would not react, so the balanced equation can be obtained by multiplying the co-efficient, on both sides by 8, that is

$$3Cu+8HNO_3=3Cu\ (NO_3)_2+2NO+4H_2O$$

II. In the reaction between Sulphur dioxide and acidified potassium dichromate solution, the unbalanced equation is

$$K_2Cr_2O_7+H_2SO_4+SO_2 \rightarrow K_2SO_4+Cr_2(SO_4)_3+H_2O$$

using Co-efficient, m,n,p,q,r and s, we can write $m\ K_2Cr_2O_7+nH_2SO_4+pSO_2=qK_2SO_4+rCr_2\ (SO_4)_3+sH_2O$.

To equalise for

(i) atoms of K ; $2m=2q$
(ii) atoms of Cr ; $2m=2r$
(iii) atoms of S ; $n+p=q+3r$
(iv) atoms of H ; $2n=2s$
(v) atoms of O ; $7m+4n+2p=4q+12r+s$

Now, let us put one of the Cœfficients, say m = 1, then from (i) and (ii), m = q = r = 1. From (iii), (iv) and (v), we find s = n = 1, and p = 3.

substitution, we have,

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

6.4. Significance of a Chemical Equation

A chemical equation gives us many informations, both qualitative as well as quantitative, regarding a chemical reaction.

1. *Qualitatively*, the equation reveals the nature of different substances involued in a chemical reaction, i.e. it tells us what substances are reactants and what are the products formed.

2. *Quantitatively*, a chemical reaction indicates (a) the proportion of the numbers of molecules of every species of reactants and products involved in the reaction.

(b) From the knowledge of the number of molecules of reactants and products, the proportions by weight of different substances of the reaction would be known.

(c) If gases are involved in the reaction, the proportions by volume of the gaseous substances may also be obtained by applying Avogadro's hypothesis.

Let us take the following example to understand the full significance of a chemical equation.

The equation $2KClO_3 = 2KCl + 3O_2$ indicates qualitatively,
$2 \times 122{\cdot}5 \quad 2 \times 74{\cdot}5, \quad 3 \times 32$

(i) that potassium chlorate decomposes to produce potassium chloride and oxygen. and its quantitative meaning,

(i) Two moles of $KClO_3$ yield two moles of KCl and three moles of oxygen.

(ii) 245 gms of $KClO_3$ gives 149 gms of KCl and 96 gms of oxygen.

(iii) 245 gms of $KClO_3$ liberates $3 \times 22{\cdot}4$ i.e., 67·2 litres of O_2 gas at N.T.P.

[∵ 1 mole of oxygen at N T P occupies 22·4 litres]

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6-5. Limitations of a chemical equation

Although a chemical equation gives us a lot of information regarding a chemical change, it still has some limitations. An equation ordinarily does not tell us :

(i) About the physical state of the reactants and products i.e., whether the substances involved in the reaction are solids, liquids, gases or solutions (dilute or concentrated).

(ii) About the energy changes accompanying the reaction, i.e., whether the reaction is exothermic or endothermic,

(iii) About the rate of reaction and the time required for its completion, i.e., whether the reaction is slow, fast or explosive.

(iv) About the reaction conditions, i.e., whether and in what way different factors, like pressure, temperature, catalyst. etc. would influence the process.

(v) Whether the reaction is reversible or goes to completion,

Notes : The above limitations can be removed as far as practicable by modifying the method of writing chemical equation by putting some indicative signs. For example :

(i) The physical states (solid, liquid, gas), of the substances involved in the reaction are indicated by putting *s*, *l*, *g* by the side of the formulæ of the participants. If the species be in solution, the sign 'aq' is used.

$$Mg\ (s) + 2HCl\ (aq) = MgCl_2\ (aq) + H_2\ (g)$$

(ii) If a solid is precipitated during the reaction, a downward arrow ↓ is placed by its side. Likewise an upward arrow ↑ indicates a gas is evolved during the process ; e.g ,

$$AgNO_3\ (aq) + KCl\ (aq) = AgCl \downarrow + KNO_3\ (aq)$$

$$2HgO\ (s) = 2Hg\ (l) + O_2 \uparrow$$

(iii) Some reactions can proceed in both directions, which are called *reversible reactions*. Such reaction are indicated with a double arrow sign ($\rightleftharpoons$) placed between the reactants and the products. e.g.,

$$NH_4Cl \rightleftharpoons NH_3 + HCl\ ;\quad 2HI \rightleftharpoons H_2 + I_2$$

(iv) To indicate the energy change associated with a chemical reaction, the quantity of heat-change that takes place, is written to the righthand side and in the same line as the equation. The heat-change is expressed in calories and shown with plus (+) sign when heat is evolved (exothermic reaction) and with (–) sign when heat is absorbed (endothermic reaction). e.g.,

$$N_2(g) + 3H_2(g) = 2NH_3\ (g) + 22200\ \text{cal}$$

$$2C(s) + H_2(g) = C_2H_2(g) - 54000\ \text{cal}$$

In modern nomenclature, this heat change is usually indicated, by the symbol 'ΔH', which is called 'enthalgy change' or 'change in heat content'. The quantity of heat change is written in the same line as the eqation but separately. In case of exothermic reaction ΔH is given a negative (–) sign and when heat is absorbed ΔH has positive (+) sign. Thus the above two reactions can be written as :

$$N_2(g) + 3H_2(g) = 2NH_3(g)\ ;\ \Delta H = -22200\ \text{cal}$$

$$2C(s) + H_2(g) = C_2H_2(g)\ ;\ \Delta H = +54000\ \text{cal}$$

6-5. Types of chemical reactions

Chemical reactions may be of different types depending on their mode of occurrence. Some of the common types of chemical reactions are summerised below.

(i) **Direct union or Synthesis :** In this type of rection a compound is formed by the direct union of the constituent elements e.g., $2H_2 + O_2 = 2H_2O$; $C + O_2 = CO_2$; $2Na + Cl_2 = 2NaCl$

(ii) **Decomposition or Analysis :** This type of reaction is the exact opposite of the first type. In this process a compound is split up into its constituent elements, either by heating or by any other process. Thus,

$$2HgO = 2Hg + O_2\ ;\ 2H_2O = 2H_2 + O_2$$

Sometimes, in this process a substance decomposes and breaks up into two or more simpler substances, i.e.,

$$CaCO_3 = CaO + CO_2\ ;\ NH_4Cl = NH_3 + HCl$$

(iii) **Double decomposition or Metathesis :** In this reaction, the constituents of the reacting compounds interchange their places and produce two new compounds. Such reactions often occur with acids, bases or salts. e.g.,

$$AgNO_3 + KCl = AgCl + KNO_3$$

$$CuSO_4 + 2KOH = Cu(OH)_2 + K_2SO_4$$

(iv) **Displacement or Substitution :** It is a process in which one element displaces another element from a compound and takes its place, such as,

$$Fe + CuSO_4 = FeSO_4 + Cu \; ; \; 2KI + Cl_2 = 2KCl + I_2$$

(v) **Hydrolysis :** In this reaction a compound reacts with water and split up, either completely or partially, to produce new substances. e.g.,

$$NH_4Cl + H_2O = NH_4OH + HCl \; ; \; PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

(vi) **Isomerism :** In this reaction, the atoms of the molecule of a compound rearrange among themselves and produce a new substance with new properties—the composition, however, remains unaltered.

$$\underset{\text{(ammonium cyanate)}}{NH_4CNO} = \underset{\text{(urea)}}{NH_2.\,CO.\,NH_2}$$

(vii) **Polymerisation :** It is a process in which two or more molecules of a compound combine together to give a new compound with higher molecular weight, which will be an integral multiple of the original one. e.g.,

$$\underset{\text{acetylene}}{3C_2H_2} = \underset{\text{benzene}}{C_6H_6} \; ; \; \underset{\text{acetaldehyde}}{3CH_3CHO} = \underset{\text{paraldehyde.}}{(CH_3CHO)_3}$$

There are many other types of reactions, such as, oxidation-reduction reactions, neutralisation reactions, additive reactions, etc., which would be discussed in their relevant sections.

Exercises—6

1. What do you mean by a chemical equation ? What does a chemical equation indicate ? Illustrate your answer with reference to the equation ; $N_2 + 3H_2 = 2NH_3$. What are its limitations ?

2, What informations can you obtain from the following equations ?

(i) $2H_2 + O_2 = 2H_2O$ (g)

(ii) $CaCO_3 = CaO + CO_2$

(iii) $2\ FeSO_4 + Ag_2SO_4 = Fe_2(SO_4)_3 + 2\ Ag$.

Show that in each the law of conservation of mass is obeyed.

3. (a) "A chemical equation does not give all informations needed for a chemical reaction"—justify.

(d) How would you express the thermal change in a chemical reaction ? Illustrate your answer giving examples of both exothermic and endothermic reactions.

4. Try to balance the following equations :

(a) $Fe_2O_3 + Al \rightarrow Al_2O_3 + Fe$

(b) $Fe + H_2O \rightarrow Fe_3O_4 + H_2$

(c) $PbS + H_2O_2 \rightarrow PbSO_4 + H_2O$

(d) $PCl_5 + H_2O \rightarrow H_3PO_4 + HCl$

(e) $Al_2O_3 + NaOH \rightarrow NaAlO_2 + H_2O$

(f) $HNO_3 + SO_2 + H_2O \rightarrow H_2SO_4 + NO$

(g) $KMnO_4 + H_2SO_4 + H_2O_2 \rightarrow K_2SO_4 + MnSO_4 + H_2O + O_2$

(h) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

5. How are the following informations symbolised in a chemical equation ?

(a) A precipitate being formed, (b) a reactant being in aqueous solution, (c) a gaseous product being evolved.

CHAPTER—VII

PHYSICAL PROPERTIES OF GASES

7-1. The Gas Laws :

A very striking fact about gases is that, they possess certain physical properties like thermal expansibility, compressibility, etc. which are found to be surprisingly indentical for all gases, irrespective of their chemical nature. The identity in behavior of different gases is evident from the fact that all gases generally obey some simple and common relations, called the *Gas Laws*, which control their physical properties. In this chapter, we shall study these laws.

7-2. Boyle's Law :

Robert Boyle (1661) extensively studied the influence of change of pressure on the volume of a gas, at constant temperature. He noticed that all gases behave alike when subjected to changes of pressure, and expressed this behavior as follows :

At a constant temperature, the volume of a given mass of any gas varies inversely as its pressure.

This is known as Boyle's law. If at constant temperature, the pressure on a gas, be doubled, the volume becomes half as great. If the pressure on the gas is reduced to one fourth, the volume becomes four times as great.

This quantitative relation between the volume of a gaseous substance and the pressure it exerts. at constant temperature can be expressed mathematically as :

$v \propto \frac{1}{P}$, when n and T are constants, where P is the pressure

v is the volume of the given mass (n moles) of gas.

$$\therefore\ v=\frac{k_1}{P} \quad \text{or,} \quad Pv=k_1 \qquad \text{............(7. 1)}$$

where k_1 is the proportionality constant.

If the same mass of gas, at constant temperature, be kept under different pressures P_1, P_2, P_3 ....such that the different volumes would be v_1, v_2, v_3 .... , then

$$Pv = P_1 v_1 = P_2 v_2 = P_3 v_3 = k_1 \qquad \text{....(7.2)}$$

(The value of the proportionality constant k_1 depends upon the mass of the gas)

Hence, according to Boyle's law, if the pressure on a given mass of a gas is altered at constant temperature, its volume changes in such a way that the product of the volume by the pressure is constant.

7-3. Charles' Law :

The influence of temprature variation on the volume of gases at constant pressure was investigated by Charles (1787) and also by Gay-Lussac (1802) independently. It was found that ; pressure remaining constant, all gases expand or contract by the same fraction of its volume at 0°C per degree change in temperature.

That is, if v_0 is the volume of the gas at 0°C

and v_t is the volume of the gas at t°C, at constant pressure,

then $v_t = v_0 + \alpha v_0 t$; or $\alpha = (v_t - v_0)/v_0 t$, where α is the fraction of v_0 by which the gas expands for 1°C rise in temperature.

Now, for all gases, α has been experimentally found to be equal to 1/273·16 or approximately 1/273.

Hence, at constant pressure, the volume of a given mass of gas increases (or contracts) by $\frac{1}{273}$ *of its volume at* 0°C *for every* °C *rise (or fall) in temperature.*

This is known as the Charles' Law. This may be expressed mathematically as,

$$v_t = v_0 + \frac{1}{273} v_0 t = v_0\left(1 + \frac{t}{273}\right) = v_0\left(\frac{t+273}{273}\right) \qquad \text{....(7.3)}$$

Where, v_0 is the volume of the gas at 0°C and v_t is the volume after the temperature has been raised to t°C. Similarly, if the gas coold to $-t$°C, then

$$v_{-t} = v_0 - \frac{1}{273} v_0 t = v_0\left(1 - \frac{t}{273}\right) = v_0\left(\frac{t-273}{273}\right) \qquad \text{..... ..(7.4).}$$

⟶

Now, if v_1 and v_2 be the volume of a given mass of a gas at temperature t_1°c and t_2°c respectively, then

$$v_1 = v_0 \frac{t_1+273}{273} \text{ and } v_2 = v_0 \frac{t_2+273}{273}.$$

$$\text{or, } \frac{v_1}{v_2} = \frac{t_1+273}{t_2+273}. \qquad \text{.... (7.5)}$$

7-4. Absolute Scale of Temperature :

If it is assumed that the gas is cooled down to -273°C, then from equation (7.4), the volume of the gas would be reduced to zero. This means that at -273°C the gas would occupy no volume. This idea is ofcourse purely hypothetical because all gases become liquid long before approaching this limit. The temperature -273°C, however affords us a very convenient reference point in thermometry, and **is** known as the *absolute zero*. A new scale of temperature with this limit as zero has been devised, in which every degree is equal to a centigrade degree. This is called the *absolute scale of temperature*, or Kelvin scale of temperature. The zero of the absolute scale is evidently -273°C and the temperature in the absolute scale is obtained by adding 273 to that in the centigrade scale. If small 't' denotes a temperature in the centigrade scale, the corresponding absolute temperature is expressed with capital 'T' and is denoted by °K. Then, $T°K = (t°C + 273)$. i.e., $0°C = 273°K$, $100°C = 373°K$, $27°C = 300°K$, $-100°C = 173°K$ add and so on.

Now, using the absolute scale, from equation (7.5), we have,

$$\frac{v_1}{v_2} = \frac{t_1+273}{t_2+273} = \frac{T_1}{T_2} \qquad \text{... (7.6)}$$

Where T_1 and T_2 are temperatures in absolute scale (°K).

(It is noted that the change in temperature by 1°C would be the same as by 1°K)

From equation (7.6), $\frac{v}{T}$ = constant, i.e, $v \propto T$ when pressure remains constant.

or, $v = k_2 T$, where k_2 is a constant. ....(7.7)

Hence, Charles' Law may be alternatively stated as :

"The volume of a given mass of gas at constant pressure is directly proportional to its absolute temperature."

The two gas laws mentioned above may be graphically represented as follow :

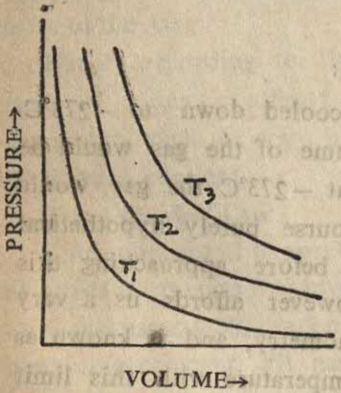

Fig. 7·1. Isothermals of Ideal gases (Boyle's Law) $T_3 > T_2 > T_1$

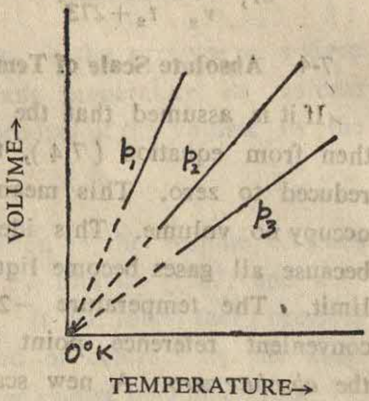

Fig. 7.2. Isobars of Ideal gases (Charle's Law) $p_3 > p_2 > p_1$

Boyle's Law is represented by plotting pressure against the volume. The curves are of rectangular hyperbola type (Fig. 7.1) and are called *isothermals* since they represent the behaviour of gases at constant temperature. Similarly Charles' Law is represented by plotting volume against absolute temperature, when we get straight lines inclined to the axes (Fig 7.2), which on extrapolation converge to zero volume indicating that the volume of a gas *theoretically* vanishes at absolute zero. These curves are called *isobars* since they refer to gases at constant pressure.

7-5. The equation of state :

The gas laws can be combined and summarised in a single equation by a well known method of algebra, giving a relation between temperature, pressure and volume of a given mass of gas.

Let P = pressure, v = volume, and T = absolute temperature of a given mass of a gas.

Then from *Boyles' Law* : $v \propto \frac{1}{P}$ when T is constant.

and from *Charls Law* : $v \propto T$ when P is constant

$$\therefore \quad v \propto \frac{1}{P} \times T, \text{ when both } P \text{ and } T \text{ vary.}$$

$$\text{or,} \quad v = \frac{T}{P} \times K, \text{ when } K \text{ is a constant,}$$

$$\text{or,} \quad \frac{Pv}{T} = K \text{ or, } Pv = KT. \qquad \text{.........(7.8)}$$

i.e., the product of pressure and volume of a given quantity of any gas is proportional to the absolute temperature. At constant temperature the product of pressure and volume (Pv) is constant. This can be shown graphically by plotting (Pv) against P at constant temp. (Fig 7.3), which gives a linear curve parallel to P-axis.

At any given temperature and pressure, the volume of a gas is proportional to the amount of the gas present and so the value of the constant K in equation (7.8), is proportional to the amount of the gas taken. Now, according to *Avogadro's hypothesis*, a gram-molecule of any gas occupies the same volume under the same conditions of temperature and pressure, and so, the value of the constant K is the same for one gram-molecule of all gases, independent of the conditions under which the gases are measured. This value of the constant K referred to per gram molecule or permole, is usually represented by R and is called the *molar gas constant* which is a universal constant. The equation (7.8) may therefore, be written as :

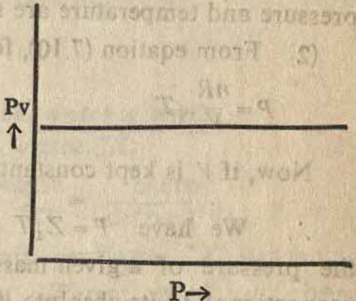

Fig. 7.3.
Pv—P isothermal

$$PV = RT, \qquad \text{........(7.9)}$$

where V is the volume of one gram-molecule of any gas under a pressure P and at an absolute temperature T. The equations of this type which correlate pressure, volume and temperature are referred to as the *equation of state.*

If n gram-molecules of the gas are to be considered, then the equation takes the from $PV = nRT$ ...... (7.10)
Where V denotes the volume of n moles of the gas. This is the most general form of the equation of state for an ideal gas, A gas that obeys this equation is called an *ideal or a perfect pas.*

Some very important and useful inferences are made from the equation of state.

(1) From euqation (7.10), for a given mass (say n moles) of a gas, $\frac{PV}{T} = nR = Z$ (constant).

If P_1, V_1, T_1 and P_2, V_2, T_2 denote the pressure, volume and temperature of a given mass of a gas at two different states,

then $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = Z$ .... (7.11)

This relation would enable us to find out the volume when pressure and temperature are simultaneously changed.

(2` From eqation (7 10), for given mass of gas,

$$P = \frac{nR}{V} . T$$

Now, if V is kept constant, then $\frac{nR}{V}$ = constant = Z_1 (say).

∴ We have $P = Z_1 T$ or $P \propto T$ when V is constant, i.e. the pressure of a given mass of gas at constant volume is directly proportional to its absolute temperature — this is another form of the Charles' Law. In fact, the pressure also increases by 1/273 of its pressure at 0°C for each °C rise in temperature.

(3) If g gm. of gas be taken, the number of gm.-moles $n = \frac{g}{M}$, where M is the molecular weight of the gas. We can write equation (7,10).

$$PV = nRT = \frac{g}{M} RT \; ; \;\; M = \frac{g}{V} . \frac{RT}{P}$$ ....(7.12)

This relation is utilised to determine the molecular weight of gas from the equation of state.

(4) From equation (7.12), we have,

$$= \frac{g}{V} . \frac{RT}{M} = d . \frac{RT}{M}, \text{ where } d = \text{density of the gas} = \frac{g}{V} ,$$

∴ for any given gas,

$$\frac{P}{dT}=\frac{R}{M}=\text{constant} \qquad \text{...........(7.13)}$$

From this relation, we have,

(a) at a constant temperature, the density of a gas is directly proportional to pressure.

(b) at a constant pressure, the density of a gas is inversely proportional to its absolute temperature.

(c) $\dfrac{P_1}{d_1T_1}=\dfrac{P_2}{d_2T_2}=\text{constant}$

(5) Evaluation of the molar gas constant 'R' :

For 1 gr-mole of a gas, equation (7.9) gives,

$$PV=RT \quad \text{or,} \quad R=\frac{PV}{T} \qquad \text{...........(7.14)}$$

Therefore, R can be evaluated by dividing the product of pressure and volume of 1 gr-mole by temperature (°K).

Now, Pressure = force/area

Volume = area × length

So, from (7.14)

$$R=\frac{PV}{T}=\frac{(\text{force/area})\times\text{area}\times\text{length}}{\text{degree }(^\circ K)}$$

$$=\frac{\text{force}\times\text{length}}{\text{degree }(^\circ K)}=\frac{\text{energy}}{\text{degree }(^\circ K)}$$

Hence R is expressed in energy units per degree (°K) per mole. The commonly used values of R in different units are given below :—

(a) In litre atmospheres :

Since 1 mole of a perfect gas occupies a volume of 22·4 litres at 0°C and 1 atm. pressure, we have $P=1$ atmosphere, $V=22{\cdot}4$ litres, $T=273^\circ K$

$$\text{Hence} \quad R=\frac{PV}{T}=\frac{1\ (\text{atm.})\times 22{\cdot}4\ (\text{litres})}{273^\circ K}$$

$$=0{\cdot}082 \text{ litre-atm. per } ^\circ K \text{ per mole....(7.15)}$$

Expressing the volume in cubic centimetres,

$$R=\frac{\text{atm})\times 22400\ \text{c.c.}}{273^\circ K}=82{\cdot}0 \text{ c.c. atm. per } ^\circ K \text{ per mole}$$

........(7.16).

(b) In C. G. S. units, (ergs) :

$P = 76$ cm of mercury $= 76 \times 13{\cdot}6 \times 981$ dynes/cm^2.

$V = 22400$ c.c. and $T = 273^\circ K$.

$$\therefore \quad R = \frac{PV}{T} = \frac{76 \times 13.6 \times 981 \text{ (dyns/cm}^2) \times 22400 \text{ c.c.}}{273^\circ K}$$

$$= 8{\cdot}314 \times 10^7 \ \frac{\text{dyne} \times \text{cm}}{\text{degree } (^\circ K)}$$

$$= 8{\cdot}314 \times 10^7 \text{ ergs per } ^\circ K \text{ per mole} \qquad \text{.... ....(7.17)}$$

Since 10^7 ergs $= 1$ Joule ; So $R = 8{\cdot}314$ Joules per °K per mole

(c) In calories (thermal units) :

Since $4{\cdot}18 \times 10^7$ ergs $= 1$ calorie

$$\therefore \quad R = \frac{8{\cdot}314 \times 10^7}{4{\cdot}18 \times 10^7} = 1{\cdot}987 \text{ calories per } ^\circ K \text{ per mole....(7.18)}$$

For approximate calcluations, $R \approx 2$ calories

Therefore, the value of R in different units are as follows :

$R = 0{\cdot}082$ litre-atmosphere per degree (K) per mole
$= 82{\cdot}0$ cc. atm. per degree (K) per mole
$= 4{\cdot}18 \times 10^7$ ergs per degree (K) per mole
$= 4{\cdot}18$ Joules per degree (K) per mole
$= 1.987$ calories per degree (K) per mole

7-6. Dalton's Law of partial pressures :

When two or more gases which do not react chemically are mixed in a vessel, each behaves as if it were alone in the containing vessel. Dalton (1801) conducted experiments to study the relation between the individual contribution of constituent gases to the over-all pressure of the gas mixture. His results are summarised in the following law :

When two or more gases, which do not react chemically, are mixed at constant temperature, each gas exerts the same pressure as if it alone occupies the whole of the containing vessel, and the total pressure exerted by the mixture is equal to the sum of the pressures exerted by each gas.

The pressure which each constituent of a gaseous mixture separately exerts is known as its partial pressure, which is obviously the pressure it would exert if it alone occupied the entire volume of the vessel at the same temperature.

Hence, Dalton's Law of partial pressure, as it is called, may be more shortly stated.

"The total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituent gases at the same temperature.

Thus, if P be the total pressure of a mixture of gases ($a, b, c, \ldots$) whose partial pressures are p_a, p_b, p_c, etc, then according to the law, $P = p_a + p_b + p_c + \ldots$ (7.19)

Let us take an illustration :

If a quantity of oxygen, which occupies 50 ml at 760 mm is placed in a 100 ml vessel, the pressure of the gas will be 380mm, provided there is no change in temperature. Similarly a quantity of nitrogen which occupies 50 ml at 760 mm will exert a pressure of 380 mm, if placed in a 100 ml vessel. However, if both the oxygen and the nitrogen, such quantities of each as occupy 50 ml at 760 mm., are placed in a 100 ml vessel, the total pressure in the vessel is found to be 760 mm, the sum of the pressures exerted by each gas when alone in the vessel, i.e., the sum of their partial pressures. This proves the law.

The relation (7.19) can be easily derived from the equation of state.

Let there be a mixture of n_a, n_b n_c........gm-moles of several gases ($a, b, c \ldots$) kept in a vessel of volume v, whose total pressure is P. The temperature T remains constant.

The total number of gm moles, $n = n_a + n_b + n_c + \ldots\ldots$

Now, form the equation of state, $P = \dfrac{nRT}{v}$ ...(7.20)

Since P is independent of the nature of the gases and depends on the net amount of the gas.

Likewise, the partial pressure of the individual constituents can also be expressed, remembering that the volume would be the same as that of the mixture and the temperature T remains constant.

Then, $p_a = \dfrac{n_a RT}{v}$, $p_b = \dfrac{n_b RT}{v}$, $p_c = \dfrac{n_c RT}{v}$ ....(7.21)

Adding the partial pressures,

$$p_a+p_b+p_c\text{......}=(n_a+n_b+n_c+\ldots)\ \frac{RT}{v}=\frac{nRT}{v}=P$$

The law is thus proved.

Now, dividing equation (7.21) by equation (7.20), we get,

$$\frac{p_a}{P}=\frac{n_a}{n}, \text{ i.e., } p_a=\frac{n_a}{n}P$$

Similarly $p_b=\frac{n_b}{n}P$; $p_c=\frac{n_c}{n}P$; and so on ....(7.22)

Now, $\frac{n_a}{n}$ represents the ratio of the number of moles of the component '*a*' present in the mixture to the total number of moles in the system, i.e., the relative amount of the component '*a*' in the mixture in terms of moles. This ratio is called the 'mol-fraction' of the component '*a*' and is expressed as x_a.

Similarly $\frac{n_b}{n}=x_b$, mol-fraction of the component '*b*' etc.

And, it is easy to see that $x_a+x_b+x_c+\ldots=1$.

That is the sum of mole fractions of all the components would be equal to unity.

Now, equations (7.22), can be written as,

$p_a=x_a\,.\,P$; $p_b=x_b\,.\,P$; $p_c=x_c\,.\,P$ and so on.

That is, "the partial pressure af a component in a gas mixture is equal to the product of its mol-fraction and the total pressure."

Mixing of gases : We shall now derive the relationship between total pressure of the gas mixture and the individual pressures (before mixing) of ths constituent gases at a constant temperature.

Let a gas occupying the volume v_1 under pressure P_1 be mixed with another gas of volume v_2 under pressure P_2.

So the total volume of the mixture $v=v_1+v_2$.

Let the total pressure of the gas mixture is P and the partial pressures of the two constituents are p_1 and p_2 repectively. So $P=p_1+p_2$.

Applying Boyles' Law to the two gases :

$$P_1 v_1 = p_1 v \text{ and } P_2 v_2 = p_2 v$$

$$\text{or, } p_1 = \frac{P_1 v_1}{v} \text{ and } p_2 = \frac{P_2 v_2}{v}$$

$$\therefore \text{ Total pressure } P = p_1 + p_2 = \frac{P_1 v_1 + P_2 v_2}{v} = \frac{P_1 v_1 + P_2 v_2}{v_1 + v_2}$$

$$\text{or, } P(v_1 + v_2) = P_1 v_1 + P_2 v_2 \qquad \text{............(7.23)}$$

Pressure of a moist gas :—Generally gases, when prepared in the laboratory, are collected over water. Hence such gases are obviously moist and saturated with water vapour. Since water vapour also contributes to the total pressure, as measured for a moist gas, the atomospheric pressure (P mm. of mercury) is equal to the sum of the partial pressure of the dry gas (p mm of mercury) and the partial pressure of the saturated water vapour, also known as aqueous tension (f mm of mercury) at the temperature at which the gas is collected.

That is, $P = p + f$; or, $p = (P - f)$.

Thus, in the cases moist gases, the value of the aqueous tension (at the temperature of the experiment) should be subtracted from the observed atmospheric pressure to determine the pressure of the dry gas.

If v c.c. be the volume of the moist gas collected at t°C, and v' cc. be the volume at N.T.P., then by the gas laws, we have,

$$\frac{v' \times 760}{273} = \frac{v(P-f)}{273+t} \text{ or, } v' = \frac{v \times (P-f) \times 273}{(273+t) \times 760} \text{cc.} \qquad \text{.......(7.24)}$$

The above expression may be used to reduce to N.T.P. the volume of a gas collected over water, where v is the observed volume of gas and water vapour, P is the barometric pressure, f is the aqueous tension at t°C.

7-7. Diffusion of gases :

The molecules of gases are not stationary ; they are always in rapid random motion in all possible directions. As a consequence, when two or more gases are brought into contact, they intermingle thoroughly and rapidly and form an intimate mixture, even against the action of gravity. Thus, if in a large room a jar of ammonia or chlorine gas be opened at one corner, its presence may be detected immediately by their characteristic odour in every part of the room, notwithstanding the facts that the room is filled with air and chlorine is much heavier then air. Similarly, if a jar filled with hydrogen is inverted over another jar full of carbondioxide, it will be noticed that the heavy CO_2 gas would move up and the very light H_2 gas would descend until the two gases are uniformly mixed up. Such spontaneous intermixing of gases without any external agency is known as diffusion of gases. The perception of the fragrance of a flower or of a perfume is possible because of diffusion of their vapour.

Thus, *gaseous diffusion is a natural process by which gaseous substances spontaneously intermingle with one another, when they are brought in contact, without the aid of outside agencies.* The diffusion is a consequence of the random motion of the gas molecules and is independent of gravity.

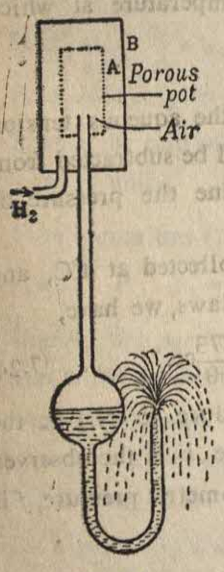

Fig. 7.4.
diffussion of gases

Different gases diffuse at different rates. Lighter gases, having lower density diffuse more quickly than heavier gases, having greater density. The fact that diffusion depends on the density of the gas may be demonstrated with the following experiment.

A small porous earthenware pot (A) is fitted with a cork to the longer limb of a narrow *U*-tube (Fig. 7.4). The tube is provided with a bulb containing some coloured liquid. The shorter limb of the U-tube is drawn into a jet. A wider jar (B) is placed inverted over the porous earthenware pot.

Now, a stream of hydrogen gas is led into the annular space between A and B when it is found that, the coloured liquid rushes out of the fine jet in the form of fountain. It occurs due to the fact that, the molecules of hydrogen, being lighter, diffuse into the pot more rapidly and therefore in larger numbers, than the molecules of air, being heavier, can diffuse out of it. In consequence the pressure inside the pot A is increased which forces out the coloured liquid as a fountain. This proves that diffusion depends on the density of the gas.

7.8. Graham's Law of diffusion :

A light gas diffuses more rapidly than a heavy gas. The relative rates of diffusion of different gases were first studied by Graham in 1829. He conducted a large number of experiments on the rates of diffusion of different gases through a porous wall under identical conditions and established a quantitative relation between the rates of diffusion and the densitis of gases. The relation is called Graham's Law of diffusion, which states as follows :

The relative rates of diffusion of different gases at the same temperature and pressure, are inversely proportional to the square root of their densities.

Mathamatically if r is the rate of diffusion and d be the density of a gas,

Then $r \propto \frac{1}{\sqrt{d}}$ or, $r = \frac{k}{\sqrt{d}}$ (k is a constant) ....(7.25)

i.e. $r \times \sqrt{d} = \text{constant}$ .... (7.26)

Consequently, $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$, where d_1 and d_2 are the densities of two gases for which the rates of diffusion under identical conditions are r_1 and r_2.

Since absolute density (d) is proportional to vapour density (D) we have, $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{D_2}{D_1}}$ ....(7.27)

For example, the relative densities (vapour densities) of hydrogen and oxygen are 1 and 16 respectively.

Therefore according to the law,

$$\frac{r_H}{r_O} = \sqrt{\frac{16}{1}} = 4 : 1$$

which means that hydrogen diffuses four times as quickly as oxygen does.

The rate of diffusion (r) means the volume rate and is expressed as number of c.c. of the gas which diffuse through a given porous wall into the air in unit time. If v c.c. of a gas diffuses out in t seconds, then

$$\text{rate of diffusion } (r) = \frac{\text{volume of diffused gas in c.c.}}{\text{time in seconds}} = \frac{v}{t} \quad \text{.... (7.28)}$$

Some of Graham's experimental results are given in the following table to establish the truth of the law of diffusion.

Gas	Density (d)	Velocity of diffusion obtained experimenially (air = 1)	$r \times \sqrt{d}$
Hydrogen	0.0695	3.830	1.01
Oxygen	1.1056	0.950	1.00
Nitrogen	0.9712	1.015	1.00
Carbondioxide	1.529	0.812	1.01
Methane	0.559	1.344	1.00

Some important and useful inferences can be deduced from Graham's law of diffusion.

(i) If v_1 and v_2 are the volumes of two gases that diffuse in times t_1 and t_2 respectively under the same condition of temperature and pressure then from equations (7.27) and (7.28), we have,

$\frac{r_1}{r_2} = \frac{v_1}{t_1} \Big/ \frac{v_2}{t_2} = \sqrt{\frac{D_2}{D_1}}$, D_1 and D_2 are the relative densities of two gases.

$$\text{or, } \frac{v_1 t_2}{v_2 t_1} = \frac{\sqrt{D_2}}{\sqrt{D_1}} \quad \text{............(7.29)}$$

Now, if $t_1 = t_2$, then from equation (7·29) $\frac{v_1}{v_2} = \sqrt{\frac{D_2}{D_1}}$ .. (7.30)

Thus under the same conditions of temperature and pressure, the volumes of gases diffusing in a given time are inversely proportional to the square root of their relative densities.

(ii) When, however, $v_1 = v_2$, the equation (7·29) gives,

$$\frac{t_2}{t_1} = \sqrt{\frac{D_2}{D_1}} \quad \text{...................(7.31)}$$

That is, the times required for two gases to diffuse by the same volume under the same temperature and pressure, are directly proportional to the square root of their relative densities.

(iii) Since, vapour density $D = \frac{1}{2}M$ (molecular weight), we have from equation (7.27),

$$\frac{r_1}{r_2} = \sqrt{\frac{D_2}{D_1}} = \sqrt{\frac{M_2/2}{M_1/2}} = \sqrt{\frac{M_2}{M_1}}$$

$$\text{or, } r \propto \frac{1}{\sqrt{M}} \qquad \text{............(7.32)}$$

Thus, the rate of diffusion of any gas is inversely proportional to the square root of its molecular weight.

7.9. Effusion of gases :

Determination of the rate of diffusion of gases being rather difficult, it is convenient to measure their rates of effusion. Effusion is the process in which a gas, confined in a practically non-porous vessel under pressure, is allowed to escape through a small aperture made in its wall. The rate of effusion has also been found to be governed by the same Graham's law of diffusion $\left(r \propto \frac{1}{\sqrt{d}}\right)$.

7.10. Practical application of the process of diffusion :

(1) Diffusion finds application in the partial separation of components in a mixture of gases of different densities—the process is called atmolysis. If the mixture is led through a tube made of porous walls, the lighter component will diffuse out more than the heavier one in a given time. As a result, the outcoming gas will contain a higher percentage of the lighter component. If the process is repeated several times, almost complete separation of components may be effected. The isotopes of neon, chlorine, oxygen etc. have been partially separated by this method.

(2) Dangers in coal mines are sometimes avoided by using Marsh Gas Alarm Indicator, which works on the process of diffusion.

(3) Vapour densities and hence the molecular weights of gases may be determined through the measurement of their rates of diffusion (or effusion). For this purpose, two gases are to be chosen, of which the molecular weight of one (M_1) is known. Then the different times, t_2 and t_1 required to effuse out same volumes of both the gases through a fine aperture under same temperature and pressure are noted. Then applying equation (7.31),

$$\frac{t_2}{t_1}=\frac{\sqrt{D_2}}{\sqrt{D_1}}=\frac{\sqrt{M_2}}{\sqrt{M_1}}, \text{ we have ,}$$

$$M_2=\left(\frac{t_2}{t_1}\right)^2\times M_1.$$

Hence the molecular weight M_2 can be obtained provided M_1 is known.

Numerical Problems :

1. A quantity of oxygen occupies a volume of 500 c.c. at 27°C. At which temperature the volume becomes double ? (pressure remaining constant).

Since P is constant, we have, $\frac{V_1}{T_1}=\frac{V_2}{T_2}$ (Charles' Law)

Hence, $V_1=500$ c.c., $V_2=1000$ c.c., $T_1=27°C$ i.e , $300°K$

$$\therefore\ T_2=\frac{V_2}{V_1}\times T_1=\frac{1000}{500}\times 300=600°K$$

$\therefore$ At 600°K the volume of oxygen will become double.

2. Half a litre of air under 360 mm. pressure is compressed to 200 ml. Taking the temperature to remain constant, find the resultant pressure.

Since T is constant, from Boyle's Law we, have, $P_1V_1=P_2V_2$,

Where, $P_1=360$ mm, $V_1=500$ c.c., $V_2=200$ c.c.

$$\therefore\ 360\times 500=P_2\times 200\ \ \therefore\ P_2=\frac{360\times 500}{200}=900\text{mm.}$$

Hence the final pressure of the gas = 900 mm.

3. Calculate the pressure exerted on the walls of a 10-litre flask containing 11·0 gm. of CO_2 gas at 27°C.

We have,

$V=10$ litres

$g=11{\cdot}0$ gm.

$M=44$

$R={\cdot}082$ lit-atm/degree

$T=27^\circ C=(27+273)=300^\circ K$

using these values in the equation

$$PV=\frac{g}{M}RT$$

or, $P=\dfrac{gRT}{VM}$, we have

$$P=\frac{11\times{\cdot}082\times300}{10\times44}=0{\cdot}615 \text{ atm}$$

4. A volume of gas together with a crystal of rock salt measures 150 c.c. at 760 mm. pressure. On raising the pressure to 1000 mm. the combined volume becomes 116·4 c.c. What is the volume of the crystal ? (temperature remains constant).

Let V c.c. be the volume of the rock salt crystal. So.

initial volume of gas $=(150-V)$ c.c.

initial pressure $=760$ m.m.

final volume of gas $=(116.4-V)$ c.c.

final pressure $=1000$ mm.

∴ By Boyle's Law, $760\times(150-V)=1000\times116{\cdot}4-V)$; on solving, $V=10$ c.c.

5. 50 c.c. of nitrogen are collected over water at 30°C and 740 mm. pressure. What will be volume of dry nitrogen at N.T.P. ? At 30°C, aqueous tension, $f=31{\cdot}6$ mm.

Since the gas is collected over water, initial pressure of dry nitrogen $=740-31{\cdot}6=708{\cdot}4$ mm.

So, $P_1=708{\cdot}4$ mm., $V_1=50$ c.c $T_1=30^\circ C=303^\circ K$

$P_2=760$ mm. $V_2=$? $T_2=273^\circ K$

∴ By the combined gas equation,

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}, \text{ we have, } \frac{708{\cdot}4\times50}{303}=\frac{760\times V_2}{273}$$

$$\text{So } V_2=\frac{708{\cdot}4\times50\times273}{303\times760}=42\text{c.c.}$$

∴ The volume of dry nitrogen at N.T.P. $=42$ c.c.

6. Oxygen is present in a 50 litre cylinder under 100 atm. pressure. How many 500 c.c. gas jars can be filled up with this oxygen at 1 atm ?

Capacity of the cylinder = 50 litres.

$\therefore$ Volume of oxygen at 1 atm. $= 50 \times 100 = 5000$ litres.

Of this total volume, 50 litres of oxygen (at 1 atm) remain in the cylinder, so that $(5000 - 50) = 4950$ litres of the gas are available for filling the gas jars of 500 c.c. capacity each.

$$\therefore \text{ No. of gas jars} = \frac{4950 \times 1000}{500} = 9900$$

7. If the density of hydrogen is 0·09 gm. per litre at N.T.P. What is its density at 15°C and 750 mm pressure ?

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ becomes } \frac{P_1}{d_1T_1} = \frac{P_2}{d_2T_2}$$

$$\therefore \frac{760}{\cdot 09 \times 273} = \frac{750}{d_2 \times (273+15)} \text{whence } d_2 = 0{\cdot}084 \text{ gm. per litre.}$$

8. A quantity of gas is contained in a spherical globe at 1 atm. If the gas is transferred to another globe with a diameter which is $\frac{1}{4}$th of the original one, what will its pressure be ? Temperature is maintained constant.

Let the diameter of the original globe be 'd', its radius will be $r = d/2$.

$\therefore$ Its volume $= \frac{4}{3}\pi r^3$.

Now, since the diameter of the second globe is $\frac{1}{4}$th of the original globe its radius also will be $\frac{1}{4}$th of the original globe

Hence the radius of the second globe $= \frac{r}{4}$.

$\therefore$ Its volume $= \frac{4}{3}\pi\left(\frac{r}{4}\right)^3 = \frac{1}{64} \cdot \frac{4}{3}\pi r^3$, i, e, the volume of the second globe is $\frac{1}{64}$ th of that of the original globe.

So, according to Boyle's law, pressure of the gas in the second globe will 64 times that of the original globe.

$\therefore$ the pressure of the gas in the second globe $= 1 \times 64$ atm.

$= 64$ atms.

9. An oxygen cylinder contains gas at a pressure of 10·3 atmosphers. It is connected with another cylinder of one-third the capacity, where the pressure is 1·1 atm. What will be the final pressure in the two vessels when the connecting tap is opened ?

Let the final pressure of the mixture be P atm.

Let the volume of 1st oxygen cylinder be v

the pressure of oxygen in 1st cylinder = 10·3 atm.

The volume of the 2nd oxygen cylinder $= \frac{1}{3}v$.

the pressure of oxygen in the 2nd cylinder = 1·1 atm.

Now, we have $P.\left(v+\frac{1}{3}v\right) = 10{\cdot}3 \times v + 1{\cdot}1 \times \frac{v}{3}$.

or, $P.\frac{4}{3}v = \left(10{\cdot}3 + \frac{1{\cdot}1}{3}\right)v$

$\therefore\ P = 8$ atmosphers.

10. A given volume of ozonised oxygen (containing 20% ozone by volume) required 175 seconds to effuse while an equal volume of oxygen took 168 seconds only under the same conditions. Find the density of ozone.

Let the volume of gas effused be v. c.c.

rate of effusion of ozonised oxygen, $r_1 = v/175$ c.c. per sec.

and rate of effusion of oxygen, $r_2 = v/168$ c.c. per sec.

By Graham's law, $\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}}$ where d_1 and d_2 are the densities of ozonised oxygen and oxygen respectively.

$\therefore\ \frac{168}{175} = \frac{\sqrt{16}}{\sqrt{d_1}}$ whence $d_1 = 17{\cdot}36$. Let the density of pure ozone be 'd'. 100 volumes of ozonised oxygen contain 20 vols of ozone and 80 vols of oxygen.

$\therefore\ 20 \times d + 80 \times 16 = 17{\cdot}36 \times 100 \qquad \therefore\ d = 22{\cdot}8$

Exercise—7

1. What is an 'equation of state' ? Establish the relation between temperature, pressure and volume of a given mass of a gas stating the laws from which the said relation is obtained.

2. Discuss the influence of temperature on the volume of a given mass of gas at constant pressure. What is absolute temperature ? Is it possible to get a temparature below absolute zero ?

3. What is 'molar gas constant' ? Why it is a universal constant ? What are its values in different units ?

4. What is meant by partial pressure ? State and explain with illustration the law of partial pressures. Derive an expression relating partial pressure of a gas in a mixture to the total pressure.

5. What is meant by gaseous diffusion. State the law that governs the rate of diffusion. Explain how diffusion may be used to calculate the molecular weight of a gas.

6. 500 c.c. of a gas is taken at N.T. P. If the pressure of the gas be reduced to 57 cm. and temperature raised to 27°C, what would be its volume ? (732·5 c.c.)

7. How much air will escape from the flask of one litre capacity if it is warmed from 25°C to 35°C, the pressure remaining constant. 33·56 c.c.

8. A sample of gas is collected at standard temperature and pressure, and the pressure is then doubled and the temperature gradually raised until the volume of the gas is the same as it was originally. At what temperature does this occur ? (273°C)

9. A flask can bear pressure upto 1·6 atm. It is filled with chlorine at 10°C and 764 mm. It is now heated till the flask explodes. At what temperature does the explosion take place ? (177·43°C)

10. A quantity of a gas together with a piece of glass meassures 100 c.c. at 27°C. When the pressure is doubled and the temperatue raised to twice the above figure, the combined volume is found to be 59·3 c.c. Find the volume of the picec of a glass. (10·55 c.c.)

11. At what temperature the density of oxygen would be the same as that of CO_2 at N.T.P. ? (198·5°K)

12. How many molecules are there in one millilitre of a perfect gas at a pressure of 1 cm. at 27°C ? ($3{\cdot}2 \times 10^{17}$)

13. A number of spherical balloons of 21 cm. diameter is to be filled ·up with hydrogen at N.T.P. from a cylinder containing the gas at 120 atmpheres and 27°C. If the cylinder can hold 2·82 litres of water, calculate the number of balloons that can be filed up, [10)

14. 110 c.c. hydrogen were colleected over water at 18°C and 740 mm pressure. Calculate the volume of the dry gas at N.T.P. (aqueous tension at 18°C = 15·4mm) (98·4 cc.)

15. Calculate the diminution in size of a toy balloon of which the volume is c.c. at 12°C and 756 mm. pressure, when taken to the bottom of a mine where the pressure is 765 mm. and the temperature 5°C. (16·3 c.c.)

16. 45gms. of electrolytic gas is contained in a 60 litre gas holder at 0°C. What is the partial pressure of each constituent ? What is the total pressure ? ($pH_2 = 0{\cdot}933$ atm ; $pO_2 = 0{\cdot}467$ atm, $P = 1{\cdot}4$ atm).

17· Calculate the partial pressures of oxygen and nitrogen in the air at 760 mm. and 0°C. Air contains 1 part of oxygen and 4 parts of nitrogen by volume. ($pO_2 = 15{\cdot}2$ cm. ; $pN_2 = 60{\cdot}8$ cm.).

18. At a constant temperature, 250 cc. of nitrogen at 720 mm. pressure and 380 cc. of oxygen at 650 mm. pressure were put in a one—litre flask. What will be the final pressure of the mixture ? (427 mm.).

19. 300 cc. oxygen required 50 seconds to escape through a porous wall. What time would 500 cc. of another gas (M = 72) require to diffuse under the same conditions ? (125 seconds)

20. The ratio of the rates of diffusion of carbondioxide and ozone is 0·29 : 0·27. The vapour density of CO_2 is 22. What is the molecular weight of ozone ? (51)

21. A gas cylinder containing cooking gas can withsand a pressure of 14·9 atmosphere. The pressure gauge of the cylinder indicats 12 atmosphers at 27°C Due to a sudden fire in the building, its temperature starts rising. At what temperature the cylinder will explode ? (99·5°C)

22. A certain gas occupies 0·418 litres at 27°C and 740 mm. pressure.

(i) What is its volume at N.T.P.

(ii) If the same gas weighs 3·00gm, what is its molecular weight ?

(0·37 litres, 181·4)

23. A straight glass tube has two inlets X and Y at the two ends. The length of the tube is 200 cm. HCl gas through inlet X and NH_3 gas through inlet Y are allowed to enter the tube at the same time. White fumes first appear at a point P inside the tube. Find the distance of P from X. (81·12 cm.).

24. When 2 gms at a gaseous substance A is introduced into an initially evacuated flask at 25°C, the pressure is found to be 1 atm. 3gm. of another gaseous subtance B is then added to it at the same temperature and pressure. The final pressure is found to be 1·5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights of A and B. (1 : 3)

CHAPTER VIII

CHEMICAL EQUIVALENTS AND ATOMIC WEIGHTS

8.1. Equivalent weight :

In chapter II, we have stated the law of equivalent proportions. It follows from the law that it is possible to assign to every element a combining weight or equivalent, which gives the relative proportion in which it combines with other elements. From careful analysis of a large number of hydrides, the weights of different elements which combine with 1·008 parts by weight of hydrogen are found as follows :

1·008 parts by weight of hydrogen combines with

(i) 3 parts by weight of carbon as in CH_4

(ii) 8 parts by weight of oxygen as in H_2O

(iii) 35·5 parts by weight of chlorine as in HCl

(iv) 23 parts by weight of sodium as in NaH

(v) 16 parts by weight of sulphur as in H_2S etc. etc.

The above data shows that 3 parts by weight of carbon or 8 parts by weight of oxygen or 35·5 parts by weight of chlorine etc.—are all chemically equivalent, because these weights of different elements have equal capabilities in converting the same weight of hydrogen (i.e. 1·008 parts by weight) into respective hydrides. Moreover, the Law of reciprocal proportions tells us that when these different elements, C, O, Cl, Ca, S etc. combine with one another, they do so in the same weight into which they combined with 1·008 parts by weight of hydrogen or in simple multiples of them.

Not only in combination, but also when one element displaces another from a compound, they do so by the same parts by weight in which they combine with 1·008 parts by weight of hydrogen. For example :

(i) In the reaction $2HCl + 2Na \rightarrow 2NaCl + H_2$;

23 gms. Na displaces 1·008 gm, of Hydrogen.

(ii) In the relation $H_2S + Cl_2 \rightarrow 2HCl + S$;

35·5 gm chlorine precipitates 16 gms of sulphur.

Thus each element has a definite combining weight or the equivalent and when elements combine together or displace one another, they do so in the ratio of these quantities or in simple multiples of them.

The number of parts by weight of an element which combines with or displaces from a compound 1·008 parts by weight of hydrogen is called its "equivalent weight" or simply "equivalent".

This defination of equivalent weight of an element was proposed by Dalton (1808) and is based on hydrogen as the standard of reference, because it has the smallest of equivalents. But since there are many elements, particularly metals, which do not form stable compounds with hydrogen, the basic standard of reference was changed to either oxygen or chlorine. On the basis of 8·000 as the equivalent weight of oxygen, the equivalent weight of hydrogen is 1·008, and that of chlorine is 35·457.

The term **'equivalent weight'** may, therefore, be defined as follows :—

The equivalent weight of an element is the number of parts by weight of that element which combines with or displaces from a compound 8 *parts by weight of oxygen, or (as secondary standards) 1·008 parts by weight of hydrogen or* 35·457 *parts by weight of chlorine.*

From this definition of equivalent weight, it is clear that when two or more elements combine, they do so in the ratio of their chemical equivalents or in simple multiples of them. This is the law of equivalent proportions already mentioned in chapter II.

Illustrations :—(i) 1·008 parts by weight of hydrogen combine with 8 parts by weight of oxygen to form water, H_2O. The equivalent weight of hydrogen, therefore, is 1·008.

(ii) 1·008 parts by weight of hydrogen combine with 35·457 parts by weight of chlorine to form hydrogen chloride. The equivalent weight of chlorine is, therefore, 35·457.

(iii) 12·16 parts by weight of magnesium displace 1·008 parts by weight of hydrogen from dilute hydrochloric acid according to the equation $Mg + 2HCl = MgCl_2 + H_2$ So 12·16 is the equivalent weight of magnesium.

(iv) In the formation of silver chloride, 35.457 parts by weight of chlorine combine with 107·88 parts by weight of silver. The equivalent weight of silver is, therefore, 107·88.

It should be remembered that the equivalent weight is only a number and has no unit. The equivalent weight of sodium is 23 ; it means that 23 gms of sodium will combine with 8 gm. of oxygen or with 35·457 gm. of chlorine. The equivalent weight of carbon is 3 ; it means 3 kg. of carbon will combine with 8 kg. of oxygen, and so on. The gram equivalent weight is the equivalent weight expressed in gram. A gram equivalent of silver is 107·88 grams of silver.

8-2. *Equivalent weight of radicals* : The concept of the equivalent of an element may be extended to radicals i.e., the number of parts by weight of a radical which combines with 1·008 parts by weight of hydrogen or its equivalent, is the equivalent weight of the radical. Some values are given below :

Compound	Composition by wt.	equivalent wt. of the radical
H_2SO_4	$H : SO_4 = 1{\cdot}008 : 48$	$SO_4 = 48$
HNO_3	$H : NO_3 = 1{\cdot}008 : 62$	$NO_3 = 62$
NH_4Cl	$NH_4 : Cl = 18 : 35{\cdot}457$	$NH_4 = 18$
Na_2CO_3	$Na : CO_3 = 23 : 30$	$CO_3 = 30.$

3-8. Equivalent weight of an element may vary :

It is necessary to point out that whereas each element possesses *one* atomic weight and (except in the cases of allotropy) *one* molecular weight, some elements possess *more than one* equivalent. When an element combines with another element to form only one compound, its equivalent weight is constant. But when an element combines with another element to give more than one compound, its equivalent weight will vary. Some illustrations are given below :

Compound	Composition by weight	Equivalent wt.
Ferrous oxide	Fe : O = 27·925 : 8	Fe = 27·925
Ferric oxide	Fe : O = 18·616 : 8	Fe = 18·616
Phosphorus trichloride	P : Cl = 10·34 : 35.457	P = 10·34
Phosphorus pentachloride	P : Cl = 6·20 : 35.457	P = 6·20
Carbondioxide	C : O = 3·00 : 8	C = 3·00
Carbonmonoxide	C : O = 6·00 : 8	C = 6·00

Such variation follows from the relationship between equivalent weight and the atomic weight, which can be deduced as follows :—

8-4. Equivalent weight and atomic weight :

Let the atomic weight, equivalent weight and valency of an element X be a, e and v respectively. Since its valency is v, one atom of X will combine with v atoms of hydrogen : the formula of its hydride is XH_v.

Therefore, $v \times 1{\cdot}008$ gm. hydrogen combine with 'a' gm. of X

or, 1·008 gm hydrogen combines with $\frac{a}{v}$ gm of X i.e., equivalent weight of the element, $e = \frac{a}{v}$

or, $a = e \times v$.

or, atomic weight = equivalent weight × valency.

i.e., Equivalent weight $= \frac{\text{Atomic weight}}{\text{Valency}}$.

Elements	At. wt.	Valency	Equivalent weight
Na	23	1	23
Mg	24	2	12
Al	27	3	9 and so on

Elements like Fe, Cu, P, etc, have variable valencies i,e. v is different in different compounds. Hence e, the equivalent weight will also be different, as the atomic weight of the element is constant.

For example, in Cu_2Cl_2, the valency of copper is 1, hence, $e=\frac{63\cdot5}{1}=63\cdot5$; but in $CuCl_2$, valency of Copper is 2, hence $e=63\cdot5/2=31\cdot75$. (the atomic weight of copper = 63.5)

8.5. Equivalent weight of a compound :

The equivalent weight of a compound is a number which shows how many parts by weight of the compound contain 1·008 parts by weight of hydrogen or the hydrogen equivalent of an active element presnt in the compound. Generally the equivalent weight of a compound is the sum of the equivalent weights of its constituent elements (or radicals). Thus the equivalent weight of $CaCO_3$ = the eq. wt. of Ca + the eq. wt. of $CO_3''=20+30=50$.

Equivalent of element or radical	Equivalent of componnd
$Ca=20$; $Cl=35\cdot457$	Calcium chloride = 58·457
$Na=23$; $NO_3=62$	Sodium nitrate = 85·00
$Ag=107\cdot88$; $Cl=35\cdot45$	Silver chloride = 143·337
$Zn=32\cdot69$; $O=8$	Zinc oxide = 40 69

A compound may often take part in more than one type of reaction, and therefore when the equivalent of a compound is stated it is normally necessary to indicate the nature of the reaction from which the equivalent is derived. Detailed discussions on eqivalent wts of acids. bases. salts and those of oxidising and reducing agents will be given in the subsequent chapters.

8.6. Determination of equivalent weights of elements :

The equivalent weight is a quantity to be determined experimentally. Different methods have been employed for the determination of equivalent weights of different elements, both metals and non-metals. The method of determination of equivalent weight of hydrogen and oxygen will be briefly described first. Then the general methods of determining the equivalents of other elements will be discussed.

8.7. Equivalent weights of hydrogen and oxygen :

Hydrogen and oxygen have been accepted as the basic standard for reference in fixing the equivalent weights of other elements.

The equivalent weight of these two elements were obtained from the most exact experiments of Morley (1895) on the gravimetric composition of water, where pure hydrogen and oxygen were allowed to burn and produce water. The weights of hydrogen, oxygen and water were accurately determined.

The combustion apparatus used by Morley consisted of three arms (Fig 8.1). The two upper arms contained the dehydrating agent P_2O_5. Pure and dry hydrogen and oxygen were weighed in large glass globes. In later experiments the hydrogen was weighed, absorbed in palladium. and driven out pure by heating. The apparatus was first completely evacuated and weighed. Sufficient quantities of the two gases (to produce about 34 grams of water) were then separately introduced into P_2O_5 tubes from the globes, and burnt therein at platinum jets at the centre of the apparatus to produce water. On combustion, the water formed collected in the lower arm of the apparatus which was kept surrounded by a freezing mixture. Any water vapour escaping upward were absorbed by P_2O_5. The residual gas was pumped out of the apparatus and analysed, and the weights of hydrogen and oxygen found were subtracted from the weights of the two gases supplied from the weighed globes. Thus the weights of hydrogen and oxygen actually burnt to water were found out. After the removal of residual gas, the apparatus was weighed—the increase in weight gave the weight of water formed.

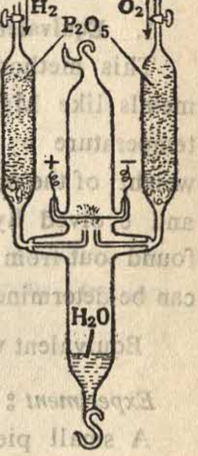

Fig. 8.1.
Morley's apparatus

Calculation : Let the wt. of H_2 admitted $= a$ gm. the wt. of O_2 admitted $= b$ gm.

wt. of residual unused $H_2 = c$ gm. the wt. of residual unused $O_2 = d$ gm.

$\therefore$ hydrogen used up $= (a - c)$ gm.

and oxygen used up $= (b - d)$ gm.

$\therefore$ In water, the ratio of wts. of H_2 and O_2 ;

$$H : O = (a-c) : (b-d).$$

Morley found that the most accurate ratio in which the two elements combined by weight was

$$O : H = 8 : 1{\cdot}008$$

These numbers have been accepted as the equivalents for hydrogen and oxygen.

8-8. General Methods of Determining the Equivalents of Elements :—

1. Equivalent weight from displacement of hydrogen

This method is applied to determine the equivalent weight of metals like Mg, Zn, Fe etc. which liberate hydrogen at room temperature by reacting with dilute mineral acids. A known weight of the metal is allowed to react with excess of dilute acid and evolved hydrogen is carefully collected and its weight is found out from its volume. The equivalent weight of the metal can be determined from the formula :

$$\text{Equivalent wt. of metal} = \frac{\text{wt. of metal} \times 1{\cdot}008}{\text{wt. of hydrogen displaced}}$$

Experiment : *Equivalent weight of magnesium*

A small piece of pure magnesium ribbon (about 0·1 gm) is carefully weighed and placed ina beaker. It is then covered with an inverted funnel and sufficient water is added till the stem of the funnel is under water. A graduated eudiometer tube filled with water is kept inverted over the stem of the funnel (Fig 8.2) and fairly strong sulphuric acid is added to water in the beaker. Quick evolution of hydrogen takes place. The envolved hydrogen collects in the graduated tube. After the metal is completely dissolved, the mouth of the

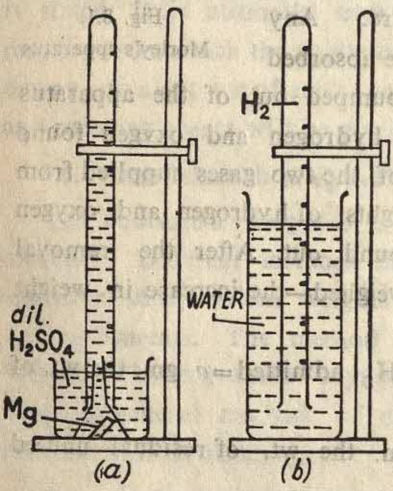

Fig. 8.2 Equivalent weight of magnesium

graduated tube is closed by the thumb and it is transferred to a tall jar full of water. The surface of water inside and outside the eudiometer tube are brought to the same level by holding the tube with a piece of paper and not with the fingers. Now the volume of the collected gas is noted, so also the temperature of water and the atmospheric pressure.

$$Mg + H_2SO_4 = MgSO_4 + H_2$$

Calculation :

Let the weight of magnesium taken $= w$ gm.

the volume of hydrogen collected $= v$ c.c.

the temperature of water $= t°c$

atmospheric pressure $= p$ mm.

Aqueous tension at $t°C$ $= f$ mm.

Since hydrogen gas is collected over water, it is moist and the atmospheric pressure = pressure of hydrogen + aqueous tension at $t°C$.

$\therefore$ pressure of hydrogen $= (p - f)$ mm.

Let v'c.c. be the volume of hydrogen at N.T.P.

Applying the Boyle's and Charles' laws, we get.

$$\frac{v \times (p-f)}{273+t} = \frac{v' \times 760}{273} \text{ or, } v' = \frac{v \times (p-f) \times 273}{(273+t) \times 760} \text{ c.c.}$$

Now 1 c.c. of hydrogen at N.T.P. weighs 0·00009 gm.

$\therefore$ Wt. of hydrogen evolved $= v' \times \cdot 00009$ gm.

That is $v' \times \cdot 00009$ gm hydrogen is expelled by w gm Mg ·

$$\therefore \text{ equivalent weight of magnesium} = \frac{w \times 1{\cdot}008}{v' \times 0{\cdot}00009}$$

$$= \frac{w \times 1{\cdot}008 \times 760 \times (273+t)}{v \times (p-f) \times 273 \times 0{\cdot}00009}$$

N.B. For determining the eq. wts. of Mg, Zn, Fe etc., dil H_2SO_4 is used, whereas in case of Al and Sn, dil HCl is used in place of dil H_2SO_4. It is necessary to add a few drops of copper sulphate solution to dil. H_2SO_4 in case of Zn, as pure Zn does not react appreciably with the acid.

∴ In water, the ratio of wts. of H_2 and O_2 ;
$H : O = (a - c) : (b - d)$.

Morley found that the most accurate ratio in which the two elements combined by weight was
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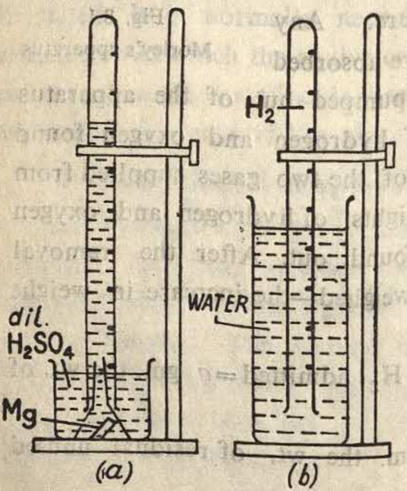

Fig. 8.2 Equivalent weight of magnesium

graduated tube is closed by the thumb and it is transferred to a tall jar full of water. The surface of water inside and outside the eudiometer tube are brought to the same level by holding the tube with a piece of paper and not with the fingers. Now the volume of the collected gas is noted, so also the temperature of water and the atmospheric pressure.

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Calculation :

Let the weight of magnesium taken $= w$ gm.

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the temperature of water $= t$°c

atmospheric pressure $= p$ mm.

Aqueous tension at t°C $= f$ mm.

Since hydrogen gas is collected over water, it is moist and the atmospheric pressure = pressure of hydrogen + aqueous tension at t°C.

$\therefore$ pressure of hydrogen $= (p-f)$ mm.

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Applying the Boyle's and Charles' laws, we get.

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That is $v' \times \cdot 00009$ gm hydrogen is expelled by w gm Mg ·

$$\therefore \text{ equivalent weight of magnesium} = \frac{w \times 1{\cdot}008}{v' \times 0{\cdot}00009}$$

$$= \frac{w \times 1{\cdot}008 \times 760 \times (273+t)}{v \times (p-f) \times 273 \times 0{\cdot}00009}.$$

N.B. For determining the eq. wts. of Mg, Zn, Fe etc., dil H_2SO_4 is used, whereas in case of Al and Sn, dil HCl is used in place of dil H_2SO_4. It is necessary to add a few drops of copper sulphate solution to dil. H_2SO_4 in case of Zn, as pure Zn does not react appreciably with the acid.

2. Equivalent weight from analysis of oxides.

(a) *By reduction of oxide.* : Many metallic oxides are reduced to metal by hydrogen, e.g., oxides of copper, iron etc, A known quantity of an oxide is reduced by heating in a stream of hydrogen and the metal formed is weighed. Hence the amount of the metal combined with 8 gm. of oxygen, i.e. its equivalent weight can be determined. The following experiment will illustrate the method.

The equivalent weight of copper. **Expt.** A small quantity of dry cupric oxide is taken in previously weighed dry porcelain boat and weighed. The weight of copper oxide, is thus known. The boat with copper-oxide is then placeed in a combustion tube, on either side of which two guard tubes containing anhydrous $CaCl_2$ are attached. (Fig 8.3). The oxide of copper is then strongly heated in a current of hydrogen, when the black oxide is reduced to the reddish metal. The water formed would be absorbed in $CaCl_2$ tube. After the completion of the reaction, the tube is cooled in a continuous stream of hydrogen. When cold the boat with the reduced copper is taken out and weighed to know the amount of copper formed. The process of heating, cooling and and weighing is repeated till the final weight is constant. This ensures completion of the reaction : $CuO + H_2 = Cu + H_2O$

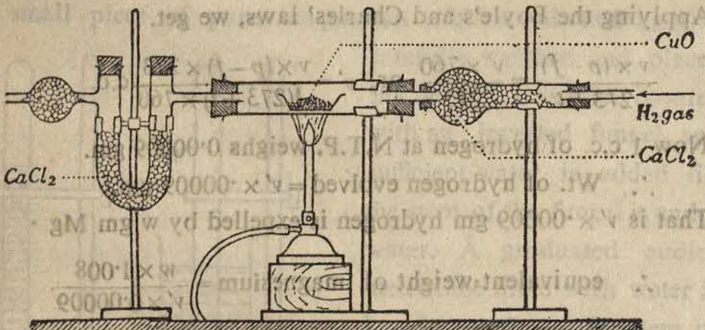


Fig. 8.3. Equivalent weight of copper by reduction method.

Calculation :

Let the weight of empty porcelain boat $= w_1$ gm.
wt. of boat + copper oxide $= w_2$ gm.
wt. of boat + copper (after expt.) $= w_3$ gm.
$\therefore$ wt. of copper $= (w_3 - w_1)$ gm.
and wt. of oxygen $= (w_2 - w_3)$ gm.

$$\therefore \text{ equivalent weight of copper} = \frac{(w_3 - w_1) \times 8}{(w_2 - w_3)}.$$

N.B. The amount of oxygen can also be obtained by weighing the amount of water formed during the combustion, which is equal to the increase in the weight of the $CaCl_2$ guard tube which absorbed the water.

(*b*) *By direct fromation of oxidc* : In this method a weighed quantity of the element is converted to oxide by heating in a current of oxygen. After cooling the oxide is weighed and the weight of the combined oxygen is found out. From this the equivalent weight of the element can be determined. This method is often unsatisfactory because the conversion to oxide is liable to be incomplete. This method has been used for the determination of the equivalents of phosphorus, carbon, and some metals like magnesium etc.

Equivalent weight of carbon.

Experiment : A known weight of pure sugar charcoal is taken in a porcelain boat and is placed in a combustion tube (Fig 8·4).

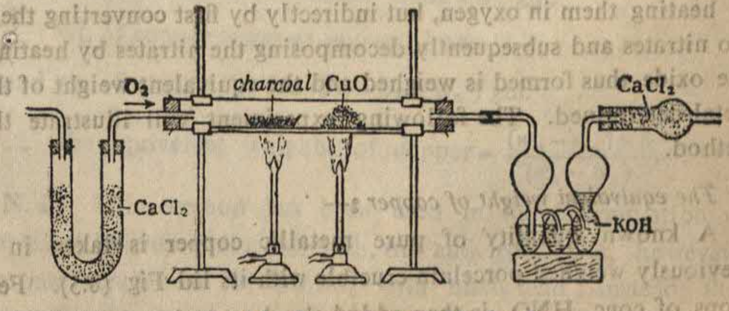


Fig. 8.4. Equivalent weight of carbon

Some quantity of copper oxide is kept in the combustion tube on the right side of the boat. Pure oxygen, dried by passing through a fused $CaCl_2$ tube is passed into the combustion tube continuously from the left side for some time to displace the air from inside the combustion tube by oxygen. A set of previously weighed potash bulbs containing conc. KOH solution is then connected to the right hand side of the combustion tube. The tube is then heated, when carbon burns into carbon-dioxide. Any trace of carbon monoxide formed would be converted into dioxide by the copper oxide. The carbon dioxide thus fromed is swept away by the oxygen gas and is absorbed in the potash bulbs. When cooled to room temperature, the potash bulbs are weighed again ; thus the amount of CO_2 formed is known.

$C+O_2=CO_2$; $CO+CuO=CO_2+Cu$.

Calculation :

Let the quantity of carbon taken $= w_1$ gm.

and the weight of carbondioxide formed $= w_2$ gm.

∴ the weight of oxygen combined with with w_1 gm. carbon $=(w_2-w_1)$ gm.

or, (w_2-w_1) gm O_2 combines with w_1 gm carbon.

or, 8·00 gm oxygen combine with $\frac{w_1 \times 8}{(w_1-w_1)}$ gm. carbon.

That is, equivalent weight of carbon $=\frac{w_1 \times 8}{(w_2-w_1)}$.

(c) *By indirect formation of oxide :*

Some metals are transformed into their oxides not directly by heating them in oxygen, but indirectly by first converting them into nitrates and subsequently decomposing the nitrates by heating. The oxide thus formed is weighed and the equivalent weight of the metal determined. The following experiment will illustrate the method.

The equivaleni weight of copper :—

A known quantity of pure metallic copper is taken in a previously weighed porcelain crucible with its lid Fig (8.5). Few drops of conc. HNO_3 is then added slowly to the metal in the crucible—a vigorous reaction takes place with the evolution of brown fumes. The whole of copper would dissolve and green copper nitrate solution would be formed. During the reaction, the crucible is nearly kept covered. The solution is then carefully evaporated to dryness on the water bath so that there is no loss of solution by spirting. The green residue left after evaporation is copper nitrate. The crucible is then strongly heated directly over a flame when the green copper nitrate is completely converted into black copper oxide. While heating, the lid is slightly put on one side in order that the evolved gases might escape. When the reaction has ceased, the crucible with its lead is allowed to cool in a desiccator and weighed again. The process of heating, cooling and weighing is repeated till the final weight is constant. The weight of copper oxide formed is thus determined.

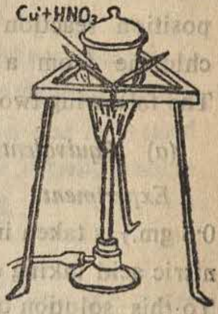


Fig. 8.5.
Equ. wt. of Copper

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

Calculation :

Let the weight of the crucible + lid = w_1 gm.

wt. of the crucible + lid + copper = w_2 gm.

wt. of the crucible + lid + cupric oxide = w_3 gm.

$\therefore$ wt. of copper taken = $(w_2 - w_1)$ gm.

and wt. of oxygen combined = $(w_3 - w_2)$ gm.

$\therefore$ the equivalent weighht of copper $= \dfrac{(w_2 - w_1) \times 8}{(w_3 - w_2)}$.

N. B. This method has been used in the determination of equivalant weights of zinc, bismuth, tin and iron. Tin, however, does not form nitrate by heating with nitric acid ; instead, the hydrated stannic oxide is obtained, which on strong heating, gives SnO_2.

3. **Equivalent weight from analysis of chlorides :**

This method involves the conversion of the metal into its chloride either directly or indirectly through double decomposition reaction using a chloride of another metal, or, replacing chlorine from a chloride by precipitation with silver nitrate. The following two examples will illustrate the method.

(*a*) *Equivalent weight of silver.*

Experiment : A weighed quantity of pure silver metal (about 0·5 gm.) is taken in a beaker and is dissolved completely in dilute nitric acid taking care to see that the solution is slightly acidic. To this solution of silver nitrate is added pure dilute hydrochloric acid in excess so that the whole of silver is precipitated as silver chloride. The precipitate is filtered through a tared filter paper, washed carefully and finally dried in an air oven at 130°C. After cooling, the dry precipitate of silver chloride is weighed.

$$Ag+2HNO_3=AgNO_3+H_2O+NO_2$$
$$AgNO_3+HCl=AgCl+HNO_3$$

Calculation : Let the wt. of silver taken $= w_1$ gm.

the wt. of silver chloride formed $= w_2$ gm.

That is, (w_2-w_1) gms. chlorine combine with w_1 gm. silver.

or, 35·457 gms of chlorine combine with $\dfrac{w_1\times 35{\cdot}457}{(w_2-w_1)}$ gm of silver.

That is, the equivalent weight of silver $=\dfrac{w_1\times 35{\cdot}457}{(w_2-w_1)}$

Alternatively : Let the equivalent weight of silver $= x$.

Then the eq. wt. of silver chloride $= x+35{\cdot}457$

(eq. wt. chlorine $= 35{\cdot}457$).

Since, 1 gm-equivalent of silver produces 1 gm-equivalent of silver chloride, we have.

$$\frac{\text{wt. of silver taken}}{\text{wt. of AgCl produced}}=\frac{\text{equivalent of silver}}{\text{equivalent of AgC}}$$

or, $\dfrac{w_1}{w_2}=\dfrac{x}{x+35{\cdot}457}$

The velue of x is then found out.

N. B. The equivalent weight of chlorine can be determined by this process if the eq. wt. of silver is known.

(b) *Equivalent weight of sodium* :

Experiment : A weighed quantity of pure sodium chloride is taken in a beaker and is dissolved completely in distilled water. The solution is made slightly acidic with nitric acid and is treated with excess of silver nitrate solution with constant stirring when a curdy white precipitate of silver chloride is formed.

$$NaCl + AgNO_3 = AgCl \downarrow + NaNO_3.$$

When further addition of silver nitrate solution forms no more precipitate, the content of the beaker is slightly heated and filtered through a tared filter paper. The precipitate is then washed with cold water, dried in an air over at 130°C, cooled in a desiccator and weighed. The processes of heating, cooling and weighing are repeated till the final weight is constant.

Calculation : Let the weight of sodium chloride $= w_1$ gm. and the wt. of silver chloride $= w_2$ gm.

We know the eq. wt. of silver is 107·88 and eq. wt. of chlorine is 35·457 and one equivalent of sodium chloride produces one equivalent of silver chloride which is $107{\cdot}88 + 35{\cdot}457 = 143{\cdot}337$ or 143·34 approximately.

Now, w_2 gms. of AgCl are produced by w_1 gm. of sodium chloride.

$\therefore$ 143·34 gms of AgCl are produed by $\frac{w_1 \times 143{\cdot}34}{w_2}$ gm of sodium chloride.

i.e., the equivalent of sodium chloride $= 143{\cdot}34 \times \frac{w_1}{w_2}$.

$$\therefore \text{ the equivalent weight of sodium} = \frac{143{\cdot}34 \times w_1}{w_2} - 35{\cdot}457$$

$$= \frac{143{\cdot}34 w_1 - 35{\cdot}457 w_2}{w_2}$$

Alternatively :

Let the equivalent weight of sodium $= x$

$$\frac{\text{Equivalent weight of sodium chloride}}{\text{Equivalent weight of silver chloride}} = \frac{\text{Weight of sodium chloride}}{\text{Weight of silver chloride}}$$

i.e. $(x+35{\cdot}457)/143{\cdot}34 = \frac{w_1}{w_2}$, $\therefore$ $x = \left(143{\cdot}34 \times \frac{w_1}{w_2}\right) - 35{\cdot}457.$

N.B. This method has been used for the determination of the equivalents of sodium, potassium, calcium, magnesium, zinc (using the bromide). lead, arsenic, silicon, iron (using the bromide) and nitrogen (as NH_4Cl).

4. Equivalent waight by replacement of one metal by another :

When a more electropositive metal displaces a less electropositive metal from its salt solution, the replacement takes place in equivalent amounts. If the equivalent of one of these two metals be known, then that of the other can be obtained.

Illustration : equivalent weight of Iron :—

Iron displaces copper from copper sulphate solution—iron dissolves and red copper is deposited .

$$CuSO_4 + Fe = FeSO_4 + Cu \downarrow$$

Experiment : A known weight of clean iron powder is gradually added into a solution of copper sulphate in a beaker. Iron gradually dissolves and red, heavy oopper powder deposits at the bottom of the beaker. It is then filtered through a previously weighed filter paper and the precipitated copper is washed thoroughly with hot water in order to remove the traces of copper sulphate. The filter paper with its contents is then dried in an air oven, cooled and weighed.

Calculation : Let the wt. of iron taken $= w_1$ gms.
and the wt. of copper displaced $= w_2$ gms.

Now, let the eq. wt. of Fe be x and the eq. wt. of copper is 31·78, We have, $\frac{\text{wt. of Cu deposited}}{\text{wt. of Fe dissolved}}=\frac{\text{eq. wt. of Cu}}{\text{eq. wt. of Fe}}$

$$\text{i.e. } \frac{w_2}{w_1}=\frac{31{\cdot}78}{x}$$

$$\therefore \quad x=\frac{31{\cdot}78\times w_1}{w_2}$$

5. Equivalent weight by the interchange of radicals :—

If one compound of a metal can be quantitatively converted into another, then the equivalent of any one of the three radicals involved can be determined, provided that the equivalents of the other two radicals are known. The method may be explained with reference to the determination of *the equivalent of fluorine*, by converting calcium fluoride into calcium sulphate by treatment with sulphuric acid.

Experiment : 1·3426 grams of calcium fluoride were treated with concentrated sulphuric acid in a platinum crucible, and the contents of the crucible were strongly heated. All the hydrofluoric acid and the excess of sulphuric acid volatilised, leaving a residue of pure calcium sulphate, according to the equation : $CaF_2+H_2SO_4=CaSO_4+2HF$.

The weight of the residual calcium sulphate was found to be 2·3421 gms.

Calculation : The ratio of the wt. of calcium fluoride taken to the weight of calcium sulphate formed must be equal to the ratio of their equivalent weights, or

$$\frac{\text{equivalent of Calcium Fluoride}}{\text{equivalent of Calcium Sulphate}}=\frac{1{\cdot}3426}{2{\cdot}3421}$$

Let the equivalent of fluorine $= x$.

Assuming the equivalent of calcium = 20·04, and that of sulphate = 48·03, we have,

$$\frac{20{\cdot}04+x}{68{\cdot}07}=\frac{1{\cdot}3426}{2{\cdot}3421}$$

$$\therefore \quad x=\left(\frac{1{\cdot}3426}{2{\cdot}3422}\times 68{\cdot}07\right)-20{\cdot}04$$

$$=39{\cdot}04-20{\cdot}04=19{\cdot}00$$

6. Equivalent weight of chlorine :

There are different ways of ascertaining the equivalent weight of chlorine.

(i) The molecular weight of hydrogen chloride has been determined very accurately which was found to be 36·465. Since the molecule contains one atom of hydrogen, the equivalent weight of chlorine is $36{\cdot}465 - 1{\cdot}008 = 35{\cdot}457$.

(ii) The weight of chlorine which combines with 1·008 parts of hydrogen was determined chemically by displacing the hydrogen in hydrogen chloride with aluminium. Let v litres of hydrogen chloride yield v' litres of hydrogen at N.T.P. and let their normal densities of N.T.P. be d and d' respectively. Hence the weights of hydrogen chloride and hydrgen are vd and $v'd'$ respectivly. Then the equivalent weight of chlorine $= \frac{vd - v'd}{v'd'} \times 1{\cdot}008$. Gary and Burt (1909) found the value to be 35·458.

7. Equivalent weight by electrolytic method :

The equivalent weight can be accurately determined from electrolysis of different compounds by the application of Faraday's laws of electrolysis. The method will be discussed in connection with the laws of eletrolysis later.

Numerical problems :

1. 3·36 gm of zinc displaced at 747·8 mm. pressure and 10·7°C, 1210 c.c. of hydrogen from dil. sulphuric acid. Calculate the equivalent weight of the metal, if the aqueous tension is 9·8 mm, at 10·7°C.

The volume of hydrogen = 1210 c.c., its temperature = 283·7°K, and its pressure $= 747{\cdot}8 - 9{\cdot}8 = 738{\cdot}0$ mm.

If v_0 be the volume of dry hydrogen at NTP, then.

$$\frac{V_0 \times 760}{263} = \frac{1210 \times 738}{283{\cdot}7} \text{ or, } V_0 = \frac{1210 \times 738 \times 273}{760 \times 283{\cdot}7}$$

$$= 1130{\cdot}66 \text{ c.c.}$$

$\therefore$ the wt. of evolved hydrogen $= 1130{\cdot}66 \times {\cdot}00009$ gm

the wt. of zinc = 3·36 gm.

$$\therefore \text{ equivalent wt. of zinc} = \frac{3{\cdot}36 \times 1{\cdot}008}{1130{\cdot}66 \times {\cdot}C0009} = 33{\cdot}28$$

2. Magnesium oxide contains 60% of magnesium. What is its equivalent weight ?

60 gm of Mg combine with 40 gm of oxygen.

$$\therefore \text{ eq. wt. of Mg} = \frac{\text{wt. of Mg} \times 8}{\text{wt. of oxygen}} = \frac{60 \times 8}{40} = 12.$$

3. The hydride of an element (at. wt. 31) contains 8·82%H_2, What is the valency of the element ?

8·82 gms of hydrogen combine with (100 − 8·82) = 91·18 gm of the element

$$\therefore \text{ the eq. wt. of element} = \frac{91{\cdot}18 \times 1{\cdot}008}{8{\cdot}82} = 10{\cdot}42.$$

$$\therefore \text{ Valency of the elements} = \frac{\text{at. wt.}}{\text{Eq. wt.}} = \frac{31}{10{\cdot}42} = 2{\cdot}98$$

i e. 3 (∵ Valency cannot be a fraction).

4. 1·62 gms of zinc were converted into nitrate by dissolving in nitric acid. The nitrate on strong heating, left 2·02 gms of the oxide. Calculate the equivalent weight of zinc.

1·62 gm of zinc produces 2·02 gm of oxide

$$\therefore \text{ wt. of oxygen} = 2{\cdot}02 - 1{\cdot}92 = 0{\cdot}40 \text{ gm.}$$

$$\text{Hence the eq. wt. of zinc } = \frac{1{\cdot}62 \times 8}{0{\cdot}4} = 32{\cdot}4.$$

5. 0·3975 gm CuO was reduced in a stream of dry hydrogen. The gaseous product was absorbed in fused $CaCl_2$ when the weight of the latter increased by 0·09 gm. What is the equvalent weight of copper ?

Amount of water formed = ·09 gm, whose $\frac{8}{9}$ th part is due to oxygen. ∴ wt. of oxygen = ·08 gm. This amount of oxygen comes from ·3975 gm of CuO,

∴ (·3975 − ·08) = ·3175 gm of copper units with ·08 gm of oxygen.

$$\text{Hence, the eg. wt. of copper} = \frac{{\cdot}3175 \times 8}{{\cdot}08} = 31{\cdot}75$$

6. One gram zinc chloride was dissolved in water. To this solution was added excess of silver nitrate when 2·110 gm silver

chloride was precipitated. The eq. wt. of Ag = 107·88. Calculate the eq. wt. of zinc.

We know, 1 gm. equivalent of zinc chloride will give 1 gm. equivalent of silver chloride by the above reaction.

Let x be the equivalent of zinc.

eq. wt. of silver = 107·88 ; eq. wt. of chlorine = 35·46.

$\therefore$ $(x+35{\cdot}46)$ gm of zinc chloride will produce $(107{\cdot}88+35{\cdot}46)$ gm of silver chloride.

But, 1 gm zinc chloride produces 2·11 gm sitver chloride.

$$\therefore \frac{1}{2{\cdot}11}=\frac{x+35{\cdot}46}{143{\cdot}34} \quad \therefore \quad x=32{\cdot}48.$$

7. The chloride of a metal M contains 47·25 percent of the metal. 1 gm of the metal would be displaced from a compound by 0·88 gm of another metal N. Find the equivalent weights of M and N.

the wt. of Metal $(M)=47{\cdot}25$ gm. $\therefore$ the wt. of chlorine = $100-47{\cdot}25=52{\cdot}75$ gm.

$$\therefore \text{ the equivalent wt. of } M=\frac{47{\cdot}25\times35{\cdot}46}{52{\cdot}75}=31{\cdot}79$$

Again, 1 gm of M displaces 0·88 gm of N $\therefore$ 31·79 gm of M will displace $(31{\cdot}79\times 88)=27{\cdot}97$ gm of N.

Hence eq. wt, of $N=27{\cdot}97$.

8. 0·14 gm iron displaced 0·1575 gm of copper from copper sulphate solution. Calculate the equivalent of copper. (equivalent of iron = 28)

From the law of equivalent proportions, if x be the equivalent of copper, then x gm of copper will be displaced by 28 gm iron.

$$\text{i.e. } \frac{x}{28}=\frac{0{\cdot}1575}{0{\cdot}14} \quad \text{Or} \quad x=31\text{-}5$$

Exercises—8

1, Explain what is meant by" equivalent weight of an element" How is the equivalent weight of an element related to its atomic weight ? State the condition under which they have the same value.

2. (a) 'The equivalent weight of an element may vary ;—Discuss.

   (b) Distinguish between "equivalent weight" and "gram equivalent weight" of an element.

3. State and explain with illustration the law of equivalent proportions. Show that this is the same as the law of reciprocal proportions,

4. Suggest a method for determining the equivalent weight of (1) Aluminium' (ii) Carbon; (iii) Sodium (iv) chlorine and (v) sulphur.

5. "The equivalent weight of an element depends on the reaction it undergoes",—Justify the statement with reference to the following pair of reactions·

   (i) $Fe + 2HCl = FeCl_2 + H_2$ (ii) $2Fe + 3Cl_2 = 2FeCl_3$

6. 0.2 gm magnesium displaced form dilute sulphuric acid 200 c.c. of moist hydrogen at 15°C and 751·5 mm, pressure. The aqueous tension is 13·5 mm. at 15°C. Calculate the aquivalent weight of magnesium. (12.07)

7. Find out the volume of hydrogen produced at N. T. P. by the action of dil. sulphuric acid on 1·45 gms of a metal whose equivalent weight is 9. [1.804 lit]

8. 0·24 gms of metal (at. wt. 24) displaces 224 cc. of dry hydrogen at N.T.P. from an acid. What is the valency of the metal ? (2)

9. An oxide of a metal contains 52·9% of the metal. Calculate its equivalent weight, (8.98)

10. The Chloride of a metal M contains 55% Chlorine. The vapour density of the chloride is 129·08. Calculate of the equivalent weight of M and the molecular formula of the chloride. (29·04, MCl_3)

11. The Chloride of an element was quantitatively converted into the corresponding oxide and the following figures were obtained : 0·1827 gm. of the chloride gave 0·1057 gm of the oxide. Calculate the equivalent of the element. (29·74)

12. 1·18 gms. Copper was dissolved in nitric acid. When the cupric nitrate formed was decomposed, it gave 1·48 gm cupric oxide. Find the equivalent weight of Copper, (31·5)

13. 10·21 gm of a metallic oxide when reduced in a current of hydrogen produced 8 gm of the metal. Show that its equivalent weight is 28·96.

14. From an aqueous solution containing 2·2 gm lead nitrate excess sulphuric acid produced a precipitate of 2·02 gm lead sulphate. The equivalent weight of SO_4 and NO_3 are 48 and 62 respectively. Find the equivalent of lead. (109·12)

15. A Solution containing 19·68 gm lithium chloride gave 66·425 gm silver chloride on preipitation with Silver nitrate. The equivalents of Silver and Chlorine are 107·9 and 35·5 respectively. Find the equivalent of lithium. (6·98)

16. 0·36 gm. of water are formed by passing dry hydrogen over 1·58 gms of heated copper oxide, when 1·26 gms. of copper are left after the experiment, calculate the equivalent weight of oxygen. (8)

17· On heating in contact with tin, sulphuretted hydrogen (density 17) is converted into hydrogen without change of volume. Calculate the equivalent weight of sulphur from this. (16)

18. 2·47 gms. of CuO were obtained by oxidising 1·986 gms of copper by nitric acid. 0·335 gm of copper was precipitated by 0·346 gms of zinc from $CuSO_4$ sulution. What are the eq. wts. of Cu and Zn ?

(Cu = 32·8 Zn = 33·87)

19. When 1·91 gm of the sulphate of a metal M is completely converted to its oxide, 1·59 gm of the latter are obtained. Find the equivalent weight of M. (31·75)

20. What weight of a metal of eq. wt. 12 will give 0·475 grm. of chloride ? (0·12 gm.]

21. When 3·565 gm of a compound MSO_4, xH_2O was heated to 100°C, it gave 2·522 gm of $MSO_4 \cdot 3H_2O$. The latter compound when further heated to 150°C gave 2·00 gm of the compound MSO_4 H_2O.

Find the equivalent of M and the value of x. (Eq. wt. = 12, x = 7)

[Hint :—(2·522—2·00) = ·522 gm corresponds to 2 mols to H_2O.

$\therefore$ (3·565 − 2·522) = 1·043 gm corresponds to $\frac{2\times1{\cdot}043}{{\cdot}522} = 4$ mols of H_2O

Hence x = 4 + 3 = 7.

3·565 gm MSO_4 $7H_2O$ 2·522 gm $MSO_4 \cdot 3H_2O$

Let e be the eq. wt. of M. $\therefore \frac{2e+96+126}{2e+96+54} = \frac{3{\cdot}565}{2{\cdot}522}$

on solving e = 12.

22. 4·215 gm. of a metallic carbonate were heated in a hard glass tube and the carbondioxide evolved was collected over mercury. It was found to measure 1336 c.c. at 700 mm. and 27°C. What was the equivalent of the metal ? (12·15)

23. A certain metal forms two oxides. When 0·5 gm of the first oxide was heated in hydrogen 0·1687 gm of water was obtained, while 0·4 gm of second oxide under similar conditions yielded 0·100 gm of water. Calculate the equivalents of the metal. [18·66, 28]

CHAPTER—IX

DETERMINATION OF ATOMIC AND MOLECULAR WEIGHTS.

9.1. Atomic Weight :

We have already seen that the atomic weight of an element gives the relative, rather than absolute weight of the atom of an element. It is the weight of an atom of the element relative to the weight of the oxygen atom taken as 16·000 (or to the weight of a carbon atom taken as 12). The knowledge of atomic weights of elements is of fundamental importance in any quantitative chemical estimation. So the determination of atomic weights, as free from error as possible, became the central problem of chemistry since the anouncement of the Dalton's Atomic Theory. Different methods are being employed to find that the atomic weights of elements. Majority of these methods give only approximate values. Nevertheless, the approximate methods do not lose their importance as the approximate atomic weight values determined by these methods are used to calculate by what whole number the equivalent weights must be multiplied in order to get the correct atomic weights. The different methods of determining atomic weights are given below :

9.2: Determination of atomic weights :

The atomic weights are usually determined by the following methods which, however, give the approximate values,

(1) Cannizzaro's method of least weight, based on Avogadro's **hypothesis.**

(2) By the application or Dulong and Petit's law of atomic **heat.**

(3) The method based on Mitscherlich's law of isomorphism.

(4) By reference to the Periodic classification.

The atomic weight of an element can be determined accurately,

(A) from equivalent weight of the element.

(B) from Stas and Richard's chemical method.

(C) from accurate molecular weight of gaseous elements.

1. **Cannizzaro's method** : This method for the determination of the atomic weight of an element has been discussed earlier. A large number of volatile compounds of the element are analysed and the least weight of the element present in a gm-mole of its compounds is accepted as the atomic weight of the element.

The method is best suitable for non-metallic elements like carbon, sulphur, nitrogen, oxygen, chlorine etc. which generally produce a wide range of volatile compounds. The method is hardly applicable for metallic elements as the metals have very few gaseous compounds.

2. **Dulong and Petit's method :**

The French Chemists Dulong and Petit in 1819 found that the atomic heat (i.e., the product of atomic weight and specific heat) for most of the solid elements was approximately 6·3 at ordinary temperature. This generalisation is known as Dulong and Petit's law.

For example, the actual atomic heat values are ;

Cu = 6·0, Pb = 6·4, Mg = 6·1, Fe = 6·1, Ag = 6·0, Ni = 6·3, etc,

Hence, according to Dulong & Petit's law,

Atomic weight × specific heat = 6·3 (approximately).

$$\therefore \text{ Atomic weight (approximate)} = \frac{6{\cdot}3}{\text{specific heat}}$$

So, an approximate value of the atomic weight of the element can be obtained from the above relationship if, however, the specific heat of the element is known.

Thus, the specific heat of magnesium = 0·262 ; hence its approximate atomic weight $= \frac{6{\cdot}3}{0{\cdot}262} = 24{\cdot}04$.

This approximate at wt. value may be converted into exact value by the method (A) described below.

N. B. Dulong and Petit's law holds true in cases of solid elements only with the exceptions of boron, carbon, silicon and beryllium where the law fails. The law is not valid for the solid elements with low atomic weights and high melting points.

3. The method based on Mitscherlich's law of isomorphism :

Chemical compounds having the same crystalline structure and exhibiting similar composition are said to be isomorphous with one another, and the phenomenon of occurrence of different chemical substances in the same crystalline form is called isomorphism. A set of common exampls are given below :

(i) Cu_2S and Ag_2S ; (ii) K_2SO_4, K_2CrO_4, and K_2SeO_4 : (iii) $ZnSO_4, 7H_2O$; $MgSO_4, 7H_2O$ and $FeSO_4, 7H_2O$, (iv) $KClO_4$ and $KMnO_4$; (v) $K_2SO_4, Al_2(SO_4)_3, 24H_2O$ (Potash alum) and $K_2SO_4, Cr_2(SO_4)_3, 24H_2O$ (chrome alum) (vi) Al_2O_3, Fe_2O_3 and Cr_2O_3 etc.

A mere similarity in the crystalline form is not sufficient test for isomorphism ; the isomorphous substances also satisfy the following two criteria ; viz.,

(i) Formation of mixed crystals.—From a solution of a mixture of isomorphous compounds (say ferrous sulphate and magnesium sulphate), homogeneous crystals separate on cooling, containing varying amounts of either substances. Such crystals are known as mixed crystals or solid solutions.

(ii) Formation of over growths.—A crystal of a substance is found to grow in size when suspended in a saturated solution of its isomorph, preserving the original crystalline shape. Thus, if a small crystal of potash alum be suspended in a solution of chrome alum the latter makes parallel deposit on the former crystal which increases in size.

Mitscherlich (1819) made a careful study of different isomorphous substances and observed that the number of atoms in two isomorphous substances was the same and one element of one compound is replaced by another element in the isomorph in equal numbers. On the basis of his observation, Mitscherlich formulated the law of isomorphism as "*substances possessing an equal number of atoms united in the same fashion exhibit identity of* *crystalline forms, which is independent of the chemical nature of the atoms but dependent upon their number and position.*"

In other words, *substances having similar chemical character and same crystalline form should have similar formulae.* An examination of the examples of isomorphous substances mentioned above would prove it.

From the examination of the isomorphous compounds the following direct consequences of the law become evident :

(i) Since isomorphous substances have similar formulae, the unknown formula of a compound can, therefore, be often found by comparison with that of an isomorphous compound of known formula. Thus the formula of potassium per chlorate is taken as $KClO_4$ as it is isomorphous with potassium permanganate $KMnO_4$ of known formula.

(ii) In isomorphous compounds, similar elements replace each other atom for atom, without disturbing the crystalline structure and the valency of the elements replacing each other must also be the same.

(iii) The weights of the two elements replacing each other are in the ratio of their atomic weights.

Let us consider a pair of isomorphous compounds in which w_1 gms of an element A (at. wt. a) in one compound replace w_2 gms of the element B (at wt. b) present in the other compound. Then in the molecule of the 1st compound, the number of atoms of $A = \frac{w_1}{a}$ and that of B in a molecule of the 2nd compound $= \frac{w_2}{b}$.

According to the law of isomorphism, one atom of A will replace one atom of B.

Therefore, we have, $\frac{w_1}{a} = \frac{w_2}{b}$ or, $\frac{w_1}{w_2} = \frac{a}{b}$

i.e. $\frac{\text{weight of the element } A}{\text{weight of the element } B} = \frac{\text{atomic weight of } A}{\text{atomic weight of } B}$

With the help of the above implications of the law of isomorphism, the atomic weight of either of the two interchangeable elements in a pair of isomorphous compouuds may be determined.

N.B. The law is generally valid but there are few exceptions. Isomorphous compounds with difference in valence or with difference in number of atoms are also known.

For example,

Ag_2S	K_2SO_4	$KClO_4$	$CaCO_3$
PbS	$(NH_4)_2SO_4$	$BaSO_4$	$NaNO_3$

4. By reference to the periodic classification :

By writing down the elements in ascending order of their atomic weights, a natural scheme was obtained by Mendeleff, in which the elements were classified in a rational manner according to their physical and chemical properties. This scheme is the periodic classification of elements. The approximate atomic weight of an element can be inferred by comparison with the atomic weights of adjacent analogous elements in the periodic table. This will be discussed more fully in Part II.

9.3. Determination of Accurate atomic weight :

(A) From equivalent weight of the element :

(i) We know that the product of the equivalent weight and the valency of an element is equal to its atomic weight, i. e.

Atomic weight = Equivalent weight × valency.

The exact atomic weight of an element is found out from the above relationship and the steps to be followed in the method are given below :

Ist step—The equivalent weight of the element under consideration is determined accurately by a chemical or an electrochemical method.

2nd step—Valency of the element cannot be directly known. It is ascertained in an indirect fashion by dividing the approximate atomic weight by equivalent weight. That is

$$\text{valency} = \frac{\text{approximate atomic weight}}{\text{Equivalent weight}}$$

The approximate atomic weight can be found out by the method based on Dulong and Petit's law or by any other suitable method discussed above. The valency thus ohtained is changed to the nearest whole number to obtain the correct valency (since valency of an element can never be a fraction),

3*rd step*—Finally, the accurate equivalent weight is multiplied by the correct valency to get the exact atomic weight.

Illustration—The equivalent weight of magnesium is found to be 12·16. Its approximate atomic weight determined by Dulong and Petit's law is 24·04. Hence the valency of magnesium $= \frac{24 \cdot 04}{12 \cdot 16}$ $= 1 \cdot 98$. But the valency cannot be 1·98, a fractional number. It must be a whole number, and we take it to be 2, the nearest integer. Hence the accurate or exact atomic weight of magnesium is $12 \cdot 16 \times 2 = 24 \cdot 32$.

(ii) Atomic weight can also be obtained easily from equivalent weight if the element has a volatile chloride. The procedure is as follows.

Suppose an element M has a volatile chloride having the formula MCl , where x is the valency of the element. Let E be the equivalent weight of the element determined accurately. The vapour density of the chloride is d, which is also found out experimentally.

The atomic weight of element $= E \times x$.

Therefore, the molecular weight of the chloride $= Ex + 35 \cdot 46x$.

Again, the molecular weight of the chloride $= 2 \times$ vap. density $= 2 \times d$.

So, we have, $Ex + 35 \cdot 46x = 2d$

$$\therefore \text{ the valency } x = \frac{2 \times d}{E + 35 \cdot 46}$$

x should be approximated to the nearest integer.

Hence, the exact atomic weight of the element $= x \times E$.

(B) **Stas and Richard's method** :—

The most accurate estimation of atomic weights has been made from chemical analysis of related compounds. The method was originally developed by Stas (1860) who carried out a large number of gravimetric estimations and established the accurate atomic weight of a large number of elements. The methods were later refined by Richards and the present day accepted values of atomic weights are mostly based on Richard's investigations.

(a) An example from Stas's experiment will explain the process. Stas carried out the following set of three experiments to find out the atomic weights of silver, potassium and chlorine.

(i) He heated a weighed quantity of $KClO_3$ and weighed the residual KCl. By difference, the amount of oxygen present in $KClO_3$ was also known. For each molecule of KCl formed, 3 atoms of oxygen were produced.

$$\therefore \text{ the ratio, } \frac{\text{wt. of KCl formed}}{\text{wt. of } O_2 \text{ produced}} = \frac{a}{48} = x \text{ (say)}$$

where 'a' = molecular wt. of KCl. Oxygen was used as standard, $O = 16$.

(ii) He precipitated a weighed quantity of KCl with excess of $AgNO_3$ solution. The precipitated AgCl was washed, dried and weighed. From the two weights the ratio of the corresponding amounts of KCl and AgCl were known.

Let the molecular weight of AgCl b 'b'.

$$\therefore \text{ the ratio, } \frac{\text{wt. of AgCl formed}}{\text{wt. of KCl used}} = \frac{b}{a} = y \text{ (say).}$$

(iii) He passed chlorine over a weighed quantity of silver, and determined the weight of AgCl produced.

Let the atomic weight of silver be 'c'.

$$\therefore \text{ the ratio, } \frac{\text{wt. of Ag taken}}{\text{wt. of AgCl formed}} = \frac{c}{b} = z \text{ (say).}$$

The three relations are

$$x = \frac{a}{48}, \quad y = \frac{b}{a}, z = \frac{c}{b}, \text{ multiplying, we get } \; xyz = \frac{c}{48}$$

or, $c = 48xyz$; and x, y, z were known from experiments performed by Stas.

Thus the atomic weight of silver was found by Stas as $c=107{\cdot}93$. Solving the equations, 'a' and 'b' were also calculated. The atomic weight of chlorine $=(b-c)$, and that of potassium $=(a-b+c)$ were also determined as $K=39{\cdot}14$ and $Cl=35{\cdot}45$.

(b) Assuming the atomic weight of nitrogen to be 14·008, the value of the atomic weight of silver was found to be 107·880 by Richards in the following way.

A weighed quantity of pure silver was dissolved in pure nitric acid. The $AgNO_3$ formed was carefully evaporated to dryness to a constant weight. The ratio of the weights of Ag : $AgNO_3$ was found as 1 : 1·5748. If the atomic weight of silver be 'a' the molecular weight of $AgNO_3$ in the oxygen scale $(O=16)=a+14{\cdot}008+48$

$$\text{Hence, } \frac{\text{at wt. of silver}}{\text{Mol. wt. of AgNO}_3}=\frac{a}{a+14{\cdot}008+48}=\frac{1}{1{\cdot}5748}$$

Solving, the value of $a=107{\cdot}880$.

(c) **Atomic weight of gaseous elements** :

The molecular weight of elementary gases can be determined with a high degree of acuracy by means of the method of limiting densities. The number of atoms present in a molecule, i,e., the atomicity is obtained by measuring the heat capacity ratio γ for the gas. For monatomic gases $\gamma=1{\cdot}66$; for diatomic gases $\gamma=1{\cdot}40$; for triatomic gases $\gamma=1{\cdot}30$, and so on.

The accurate atomic weight may be obtained by dividing the the molecular weight by atomicity,

i.e. the atomic weight of a gaseous element

$$=\frac{\text{molecular weight of the gas}}{\text{atomicity}}$$

For example : the molecular weight of nitrogen is 28·01 and its $\gamma=1{\cdot}41$. Hence its atomicity = 2.

$$\therefore \text{ the atomic weight of nitirogen}=\frac{28{\cdot}01}{2}=14{\cdot}005.$$

9.4. **Molecular weight** : Molecular weight of a substance is the sum of atomic weights of all constituent elements ; it is, therefore, expressed on the same scale as the atomic weight. The molecular weight of a substance gives the relative weight of the molecule of a substance, it is the weight of a molecular of the substance relative to the weight of the oxygen atom as 16·000 (or the weight of a carbon atom as 12·000).

9-5. Determination of molecular weight :

It has already been discussed that the molecular weight of a substance can be obtained simply by adding the atomic weights of the constituent atoms, provided the molecular formula of the substance is known. The experimental method of determination of the molecular weight of a gas or vapour is grounded on the observation of its density. The normal density of a gas is the weight of 1 litre of the gas at **N.T.P.** The normal density of hydrogen is 0·0899 gm. or 0·09 gm. approximately. The relative

$$\text{density of a gas} = \frac{\text{normal density of gas}}{\text{normal density of H}_2} = \frac{\text{normal density of gas}}{0{\cdot}09}$$

$\therefore$ normal density of a gas = relative density × 0·09.

From Avogadro's hypothesis, we have seen that molecular weight of a gas = 2·016 × relative density.

Suppose M = molecular weight of a gas and D is the normal density. Then we have,

$$\frac{M}{2{\cdot}016} \times {\cdot}09 = D \text{ or, } M = \frac{2{\cdot}016}{{\cdot}09} \times D$$

$$\text{i.e. } M = 22{\cdot}4 \times D$$

$$\text{and also } M = 2{\cdot}016 \times \text{relative density.}$$

Hence the molecular weight of a gaseous substance or a volatile liquid can be determined from density measurements with the help of the following relations :

(i) $M = 2{\cdot}016 \times$ relative density (vapour density)

(ii) $M = 22{\cdot}4 \times D$, where D = normal density.

(iii) $M = \frac{gRT}{PV}$, from the gas equation $PV = nRT = \frac{g}{M}RT$.

Where P = pressure in atomosphere ; V = volume in litres ; g = weight of the substance in grams ; $R = 0{\cdot}082$ litre atomsphere ; T = temperature in absolute scale.

There are various methods of determining the density of a gas. But the most convenient method of determining the density of a vapour is that devised by Victor Meyer (1878).

Victor Meyer's method : Relative density, hence the molecular weight of a volatile liquid is generally determined by this method. In this method the vapour of a volatile substance is caused to displace its own volume of air which is collected and meassured under the physical conditions of the room. The apparatus (Fig 9·1) is a long glass tube with a bulb blown at the bottom and having a side tube. At first the apparatus is carefully cleaned and dried. The open end of the tube is then closed by a rubber cork, and the apparatus is placed in a wider copper jacket in which a liquid boils —its boiling point being about 25° higher than that of the liquid which is about to be vaporised. The end of the side tube now dips under water in a trough. Air expelled by the thermal expansion of the air in the apparatus bubbles out of the side tube. When no further bubble escapes, the apparatus is ready for use. A graduated tube filled with water is inverted over the side tube, and a small sloppered bottle containing a known weight of the liquid (about 0·1gm) is quickly dropped into the apparatus (a little sand or asbestos may be put in the bulb to avoid fracture) by removing the rubber cork. The cork is quickly replaced. The stopper of the bottle opens and the liquid vaporises quickly—the vapour displacing an equal volume of air which is collected in the graduated tube by the displacement of

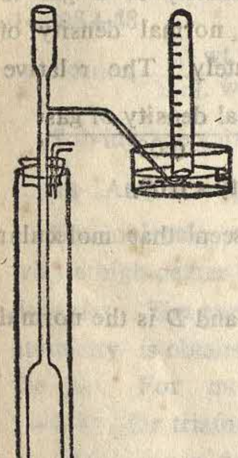


Fig. 9·1 Victor Meyers' apparatus

water. When no more air issues from the side tube, the graduated tube is closed with the thumb and is allowed to stand submerged in a tall jar of water until it has attained the temperature of water. Then it is raised so that the levels of water inside and outside are the same, and the volume of the displaced air is noted. The temperature of water and the atmospheric pressure are also noted.

Calculation : Let, the weight of the substance $= g$ gm ; Volume of the air displaced $= v$ cc. Barometric pressure $= P$ mm. Temperature of water $= t°c$, Aqueous tension at $t°c = f$ mm. If v' cc. be the volume of air at N. T. P., then

$$v' = \frac{v\ (p-f) \times 273}{(273+t) \times 760} \text{ cc.} \qquad \text{(vide equation 7·24)}$$

Weight of an equal volume of hydrogen $= v' \times 0{\cdot}00009$ gm.

$$\therefore \text{ relative (vapour) density} = \frac{g}{v' \times 0{\cdot}00009}.$$

Hence the molecular weight of the substance can be calculated by using any one of the three relations mentioned above.

Numerical Problems :

1. 5·01 gm. of a metalic oxide on reduction by hydrogen produced 4·41 gm. of the metal. The specifie heat of the metal is 0·055. What is the atomic weight of the metal ?

$(5{\cdot}01 - 4{\cdot}41) = 0{\cdot}6$ gm O_2 combines with 4·41 gm metal.

$$\therefore \text{ Eq. wt. of metal} = \frac{4{\cdot}41 \times 8}{0{\cdot}6} = 58{\cdot}8.$$

$$\text{The approx. at. wt. of the metal} = \frac{6{\cdot}3}{{\cdot}055} = 114{\cdot}55$$

Hence the valency is $\frac{114{\cdot}55}{58{\cdot}8} = 1{\cdot}95 \approx 2$. (nearest whole number

$\because$ valency cannot be a fraction).

Therefore, the exact atomic wt. $= 2 \times 58{\cdot}8 = 117{\cdot}6$.

2. 0·125 gm. of a metalic chloride was formed form 0.054 gm of the metal, whose specific heat is 0·241. Find out the atomic weight of the metal.

$(\cdot 125-\cdot 054)=\cdot 071$ gm of chlorine combine with ·054 gm metal.

$\therefore$ the eq. wt. of the metal $=\dfrac{0\cdot 54\times 35\cdot 46}{\cdot 071}=26\cdot 97.$

By Dulong & Petit's law,

The approx at. wt. of the metal $=6\cdot 3/\cdot 241=26\cdot 14,$

Hence the valency is $\dfrac{26\cdot 14}{26\cdot 97}=0\cdot 969\approx 1$ (nearest whole number)

Therefore the exact. at. wt. $=26\cdot 97.$

3. Find the atomic weight of a metal, *M* whose equivalent weight is 29·73 and the vapour density of its chloride is 8·16 $(O=1)$.

Let x be the valency of the metal; then its chloride is MCl_x. The vap. density of its chloride $=8\cdot 16\times 16\ (H=1)=130\cdot 56.$

$\therefore$ The mol wt. of the chloride $=a+35\cdot 5x=2\times 130\cdot 56=261\cdot 12,$ where a is the atomic weight of the metal.

Now $a=29\cdot 73\times x$

$\therefore\ 29\cdot 73\times x+35\cdot 5x=261\cdot 12$

or, $x\,(65\cdot 23)=521\cdot 6\quad \therefore\ x=\dfrac{261\cdot 12}{65\cdot 23}=4\cdot 003\approx 4$

So the at. wt. of $M=29\cdot 73\times 4=118\cdot 22.$

4. The equivalent weight of a volatile metal is 100·3. The specific heat of the metal is 0·033; 0·25 gm. of the metal occupies 79·5 cc. at 500°c and 760 mm. Calculate the atomic weight of the metal and the molecular weight of the vapour, Indicate the atomicity of the vapour.

The approx. at. wt. of the metal $=6\cdot 3/\cdot 033=190\cdot 9.$

$\therefore$ the valency of the metal $=\dfrac{190\cdot 9}{100\cdot 3}=1\cdot 9\approx 2.$

Hence the accurate at. wt. of the metal $=100\cdot 3\times 2=200\cdot 6$

We know $PV=\dfrac{g}{M}RT$ or, $M=\dfrac{gRT}{PV}.$

$$\text{i.e. Mol. wt. of the vapour} = \frac{\cdot25 \times \cdot082\ (\text{lit-atm}) \times 773\ (^\circ K)}{1\ (\text{atm}) \times \cdot0795\ (\text{lit})}$$

$$= 199{\cdot}5.$$

Hence the atomicity of vapour = 1 i.e. the vap. is monatomic.

5. A metal *M* which is divalent in its ordinary salts, forms an oxide which contains 90·66% of the metal. When 13·70 gm. of its oxide were treated with nitric acid, 13·24 gm. of the nitrate were formed, and an insoluble residue weighing 4·78 gm. was left. The residue was shown by analysis to be another oxide of *M* containing 86·61% *M*. From these data calculate the atomic wt. of *M* and write down the formulae of the two oxides.

13·24 gm of nitrate formed form (13·70 – 4·78) = 8·92 gm. of the metallic oxide.

i.e., metallic oxide→metallic nitrate

Let the equivalent of the metal = e ; of oxygen = 8, of nitrate = 62.

$$\therefore \quad \frac{e+8}{e+62} = \frac{8{\cdot}92}{13{\cdot}24} \text{ whence } e = 103{\cdot}65.$$

Since the metal is normally divalent, its at. wt. = 103·65 × 2 = 207·3.

1st oxide $M : O = 90{\cdot}66 : 9{\cdot}34$

∴ atoms of M : atoms of O

$$= \frac{90{\cdot}66}{207{\cdot}3} : \frac{9{\cdot}34}{16} = 3 : 4$$

∴ the formula is M_3O_4.

2nd oxide (insoluble residue)

$M : O = 86{\cdot}61 : 13{\cdot}39$

$$\therefore \frac{\text{atom of } M}{\text{atom of } O} = \frac{86{\cdot}61/207{\cdot}3}{13{\cdot}39/16} = \tfrac{1}{2}$$

∴ the formula is MO_2.

5. **Potassium permanganate contains 34·8% Mn. It is isomorphous with potassium chlorate $KClO_4$. Find the atomic weight of manganese.**

Let x be the atomic weight of manganese.

The formula of potassium permanganate is $KMnO_4$ as it is isomorphous with $KClO_4$.

So the mol. wt. of $KMnO_4 = 39 + x + 4 \times 16 = 103 + x$

$$\text{and \% of Mn in the compound} = \frac{x \times 100}{103 + x}.$$

According to the data supplied,

$$\frac{x \times 100}{103 + x} = 34{\cdot}8 \quad \therefore \quad x = 54{\cdot}98.$$

7. Cu_2S and Ag_2S are isomorphous compounds. The percentage of sulphur in the former is 20·14 and in the latter 12·94. The at. wt. of Cu is 63·57, calculate the at. wt. of Ag.

In Cu_2S : $(100 - 20{\cdot}14) = 79{\cdot}86$ gm of Cu combine with 20·14 gm of sulphur.

In Ag_2S : $(100 - 12{\cdot}94) = 87{\cdot}06$ gm of Ag combine with 12·94 gm of sulphur.

or, $\dfrac{86{\cdot}06 \times 20{\cdot}14}{12{\cdot}94} = 135{\cdot}5$ gm of Ag unite with 20·14 gm of sulphur

$$\therefore \quad \frac{\text{At. wt. of Ag}}{\text{At. wt. of Cu}} = \frac{135{\cdot}5}{79{\cdot}86}$$

$$\therefore \quad \text{At. wt. of Ag} = \frac{135{\cdot}5}{79{\cdot}86} \times 63{\cdot}57$$

$$= 107{\cdot}86.$$

8. 0·22 gm. of a substance when vaporised in Victor Meyer's apparatus displaced 45 cc. of air collected over water at 20°C and 755 mm. pressure. Calculate the molecular weight of the substance. (aqueous tension '*f*' at 20°C = 17·4 mm.)

1st method : volume of vapour = volume of air displaced. Let v be vol. at N.T.P.

$$\therefore \frac{760 \times v}{273} = \frac{(755 - 17{\cdot}4) \times 45}{293} \quad \text{or,} \quad v = 40{\cdot}81 \text{ cc.}$$

40·81 cc. at NTP weigh 0·22 gm.

$$\therefore \quad 22{\cdot}4 \text{ litres at N.T.P. weigh } \frac{0{\cdot}22 \times 22{\cdot}4}{{\cdot}04081} = 120{\cdot}7 \text{ gm.}$$

$$\therefore \quad \text{the mol. wt.} = 120{\cdot}7.$$

2nd Method :—

we know, $(p-f)v=\frac{g}{M}RT$

$$\text{or, } M=\frac{gRT}{(p-f)\times v}=\frac{0{\cdot}22\times0{\cdot}082\times293\times760}{737{\cdot}6\times{\cdot}045}$$

$$\therefore\ M=120{\cdot}7.$$

$[p-f=755-17{\cdot}4=737{\cdot}6\text{ mm.}=\frac{737{\cdot}6}{760}\text{ atm.}$

$v=45\text{ c.c}={\cdot}045\text{ lit.}]$

Exercise—9

1. Show how would you proceed to find out the atomic weight of Carbon by Cannizzaro's method. Does the method give corrcet atomic weight value? How do you obtain the exact value of atomic weight from the aproximate value?

2. Obtain the relation between the atomic weitght and the equivalent weight of an element.

3. State Dulong-petit's law. Explain its applicaiton in the determination of atomie weights of elements. State the limitations of this proeess.

4. How would you proceed to determine the exaet atomie weight of an element?

5. (a) State Mitscherlich's law of isomorphism and explain how it helps to the determination of atomic weights.
   (b) What are isomorphors substances? Give examples. (c) What are the criteria of isomorphism?

6. Explain what is meant by (a) molecular weight, (b) vapour density. What is the relation between the two? Describe a method for the determination of the moleular weight of a volatile liquid

7. Vapour density of three substances referred to hydrogen as unity, were 45, 70 and 25 respcetively and the percentages by weight of a certain element contained in each were 22·22, 42·86 and 40 respcetively. what is the probable value of the atomic weight of the element? (20)

8. The chloride of a metal contains 20·2% of the metal. Find out its atomic weight if the specific heat of the metal be 0·224. The vapour density of the chloride is 133 (H=1), what is its molecular formula. (26·94, M_2Cl_6).

9. One gram of a metal displaced from H_2SQ_4 1242 cc. of dry hydrogen gas at N·T.P. The Specific heat of the metal is 0·238. Find out the exact atomic weight of the metal. (26·97)

10. The vapour density of the chloride of an element M is 66 and the oxide of the element contains 54% of the element. Calculate the atomic weight of M. (27)

11. If the equivalent weight of a metal M be x and the formula of its oxide be $M_p O_q$, show that the atomic weight of $M = \frac{2xq}{p}$.

12. 10 gms of mercury unite with 0·8 gm of oxygen to form an oxide. 1000 cc. of mercury vapour at N.T.P. weigh 8·923 gm. The specific heat of mercury is 0·033. Use these data to show that mercury molecules are monatomic.

13. 0·1755 gm of a bivalent metal and 0·1316 gm of a trivalent metal, when separately placed in dil. HCl, yield the same volume of hydrogen, viz, 190 c.c. at 27 cc and 720 mm. pressure. Find the atomic weights of the metals. (24, 27)

14. The calculation of isotopic abundance by a mass spectographic analysis show that ordinary carbon is a mixture of 2 isotopes, 98·892%C^{12} and 1·108%C^{13} C^{12} has a mass of 12·0 and C^{13} has a mass of 13.00335. Calculate the atomic weight of Carbon. (12·0111

15. 0·51 gm. $AgNO_3$ was required to precipitate the chlorine from 0·22 gm) of a metallic chloride. What is the atomic weight of the metal if its specific heat be 0·057 ? (Equivalent weight of silver = 107·88) (113·5)

16. A metal forms two oxides, containing respectively 22·2 and 30 percent of oxygen. Its specific heat is 0·114. What formula would you assign to them ? (MO, M_2O_3)

17. An element X forms a chloride which is isomorphous with potassium chloride and contains 25·87% chlorine. calculate the atomic weight of X. (101·7)

18. The oxides of two metals A and B are isomorphous. The atomic weight of A is 52 and forms a chloride whose Vapour density is 79. The oxide of the metal B contains 47·1% oxygen. Calculate the atomic weight of B. (27)

19. Chrome alum and potash alum are isomorphous and contain 10·42% chromium and 5·70% aluminium respectively. Calculate the atomic weight of chromium, that of aluminium = 27. (52)

20. By converting pure silver into silver nitrate, Richards found the ratio Ag ; $AgNO_3$ = 1 : 1·57479. Calculate the atomic weight of silver, assuming that for nitrogen to be 14·008 (107·88)

21. 0·6 gm of a volatile substance displaces 123 cc. of moist air at 20°C and 757·5 mm. Find the vapour density and molecular weight of the substance (aqueous tension at 20°C = 17·5 mm) (59·79, 119·58)

22. 250 cc. of a gas at N.T. P. weigh 0·7317 gm. Density of hydrogen at N. T. P is 0·08987 gm/lit. What is the vapour density of the gas . Determine its molecular weight. (32·56, 65·13).

CHAPTER—X

CHEMICAL CALCULATIONS

Stoichiometric Calculation :

The most important aspect of a chemieal equation is its quantitative significance which has already been discussed. A chemical equation indicates the relative amounts by weight (also by volume in case of gases) of different substances participating in the chemical reaction. We can therefore easily find out, from a correctly balanced equation, what amount of products would be available from the given reactants and vice versa. In order to solve problems based on chemical equations, it is necessary to remember some basic facts, already discussed in previous chapters.

(i) Molecular weight is the sum of the atomic weights of the constituent atoms.

(ii) Atoms and molecules stand for gram-atoms and gram-molecules, i.e., atomic weight and molecular weight expressed in grams.

(iii) The density of hydrogen is 0·09 gm/litre at N.T.P.

(iv) Molecular weight of a gas = 2 × vapour density.

(v) One mole (i.e., one gram-molecular weight) of a gas occupies 22·4 litres at N.T.P.

(vi) The gas equation relation : $P_1V_1/T_2 = P_2V_2/T_2$

(vii) atmomic weight = equivalent wt. × valency.

Besides, all reactions represented by chemical equations are assumed to take place at N.T.P., i.e., at 0°C and 760 mm. pressure, if otherwise not mentioned.

The problems that may arise from the information based on a chemical equation, may be classified as follous :—

(i) Problems based on weight to weight relations.
(ii) . . .... weight to volume relations.
(iii) .... volume to volume relation.

10-1. **Problems on weight to weight relations :**

Method—1. Correct equation representing the chemical reaction is to be written,

2. The relative weights of the substances are to be noted down below their formulae.

3. The weights are relative, the same unit is to be used throughout the process of calculation.

Problem 1. Find the weight of quicklime obtained by strongly heating 40 gms. of marble. $(Ca=40)$

$$\begin{array}{lll} CaCO_3 & = & CaO + CO_2 \\ (40+12+48) & & 40+16 \\ =100 & & =56 \end{array}$$

100 gms. of marble on being strongly heated yield 56 gm of quicklime.

∴ 40 gms of marble will yield $\frac{56 \times 40}{100} = 22{\cdot}4$ gms. of quicklime.

Problem 2. How much $KClO_3$ would have been decomposed to produce 1 kg of oxygen ? $(K=39)$

$$\begin{array}{ll} 2KClO_3 & =2KCl+3O_2 \\ 2[39+35{\cdot}5+48] & 3\times 32=96 \\ =245 & \end{array}$$

96 gms oxygen are obtained from 245 gms $KClO_3$

Hence 1 kg i.e. 1000 gm oxygen are obtained from $\frac{245 \times 1000}{96}$ gms $KClO_3 = 2{\cdot}552$ kg $KClO_3$.

Problem 3. How much sulphuric acid will be required to dissolve 13 gms of Zinc completly ? What amount of Zinc Sulphate will be produced ? $(Zn=65{\cdot}3)$

$$\begin{array}{ccccccc} Zn & + & H_2SO_4 & = & ZnSO_4 & + & H_2 \\ 65{\cdot}3 & & 2+32+64 & & 65{\cdot}3+32+64 & & \\ & & =98 & & =161{\cdot}3 & & \end{array}$$

65·3 gms Zn is dissolved in 98 gms H_2SO_4

∴ 13 gms Zn will be dissolved in $\frac{98 \times 13}{65{\cdot}3}$ gms H_2SO_0

$= 19{\cdot}51$ gms H_2SO_4.

Again, 65·3 gms Zinc produce 161·3 gms $ZnSO_4$.

$\therefore$ 13 gms Zinc will produce $\dfrac{161\cdot3 \times 13}{65\cdot3}$ gm $ZnSO_4$

$= 32\cdot11$ gm. $ZnSO_4$

Problem 4. Find the weight of Calcium nitrate formed by treating 60 gms. of calcium oxide with 100 gms of nitric acid. (Ca = 40)

$$\begin{array}{llll} CaO \;+ & 2HNO_3 & = \; Ca(NO_3)_2 & + \; H_2O \\ 40+16 & 2(1+14+48) & \;\;\; 40+2(62) & \\ =56 & =126 & \;\;\; =164 & \end{array}$$

56 gms CaO react with 126 gms HNO_3

$\therefore$ 60 gms CaO will react with $\dfrac{126 \times 60}{56} = 135$ gms HNO_3.

But the weight of HNO_3 given is 100 gms. which is in deficit. The whole amount of CaO will not therefore react, a portion of it will be left in excess. So, the weight of Calcium nitrate formed during reaction will definitly depend upon the reactant which is in deficit, i.e., on the weight of HNO_3, because the reaction will stop as soon as HNO_3 is exhausted.

Now 126 gm HNO_3 will produee 164 gm $Ca(NO_3)_2$

$\therefore$ 100 gm HNO_3 will produce $\dfrac{164 \times 100}{126} = 130\cdot16$ gm

$Ca(NO_3)_2$

That is 130·16 gm $Ca(NO_3)_2$ will be formed.

Problem 5. What quantity of Zinc will be required to produce from sulphuric acid the same amount of hydrogen as obtained from 130 gms aluminium reacting with Caustic Soda solution ? (Al = 27, Zn = 65.

$$\begin{array}{lll} \text{Eqns : (i)} & 2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2 \\ & 2 \times 27 = 54 \qquad\qquad\qquad\qquad\qquad 3 \times 2 = 6 \\ \text{(ii)} & Zn + H_2SO_4 \quad = ZnSO_4 + H_2 \\ & 65 \qquad\qquad\qquad\qquad\quad 2 \end{array}$$

Thus, 54 gms Al can produce 6 gms hydrogen.

$\therefore$ 135 gms Al can produce $\dfrac{6 \times 135}{54} = 15$ gms hydrogen

But, 2 gms hydrogen can be produced by 65 gm Zinc.

So, 15 gms hydrogen can be produced by $\frac{65 \times 15}{2} = 487{\cdot}5$ gms Zinc.

That is 487·5 gms Zinc will be required.

6. 80 gms of $KClO_3$ are heated to produce oxygen. Hydrogen is generated by the action of H_2SO_4 on Zn. What weight of Zinc will be required to generate sufficient hydrogen to completly combine with the oxygen obtained from the $KClO_3$? (K = 39, Zn = 65)

$$\begin{array}{lcl} 2KClO_3 & = & 2KCl \;\; +3O_2 \\ 2(39+35{\cdot}5+48) & & \;\;\;\;\;\;\;\; 3\times 32 \\ = \;\; 245 & & \;\;\;\;\;\;\;\; = 96 \end{array}$$

$$\begin{array}{lcl} Zn+H_2SO_4 & = & ZnSO_4 \;\; +H_2 \\ 65 & & \;\;\;\;\;\;\;\;\;\;\;\; 2 \end{array}$$

245 gms $KClO_3$ can produce 96 gm oxygen.

∴ 80 gms $KClO_3$ can produce $\frac{96 \times 80}{245} = 31{\cdot}35$ gm oxygen

$$\begin{array}{lcl} 2H_2 & + & O_2 = 2H_2O \\ 2\times 2 & & 32 \\ = 4 & & \end{array}$$

Now 32 gm Oxygen combine completly with 4 gm Hydrogen:

∴ 31·35 gms oxygen combine with $\frac{4 \times 31{\cdot}35}{32} = 3{\cdot}92$ gm Hydrogen.

But, 2 gms Hydrogen can be produced by 65 gms Zinc.

∴ 3·92 gms Hydrogen can be produced by $\frac{65 \times 3{\cdot}92}{2}$

$= 127{\cdot}4$ gms Zinc.

7. 1·84 gms of a mixture of $CaCO_3$ and $MgCO_3$ are strongly heated till no further loss in weight takes place. The residue left weighs 0·96 gm. Calculate the percentage composition of the mixture, (Ca = 40, Mg = 24).

Let the amount of $CaCO_3$ present be x gm. ∴ the amount of $MgCO_3$ would be $(1{\cdot}84 - x)$ gm.

Now. (i) $CaCO_3 = CaO + COn \uparrow$

$40+12+48 \qquad 40+16$

$=100 \qquad =56$

(ii) $MgCO_3 = MgO + CO_2 \uparrow$

$24+12+48 \quad 24+16$

$=84 \qquad =40$

from (i) 100 gms $CaCO_3$ gives a residue of 56 gms CaO

$\therefore$ x gm $CaCo_3$ gives a residue of $\frac{56x}{100}$ gms CaO

from (ii) 84 gms $MgCO_3$ gives a residue of 40 gms MgO

$\therefore$ $(1{\cdot}84-x)$ gms $MgCO_3$ gives a residue of

$\frac{40\,(1{\cdot}84-x)}{84}$ gms MgO.

$\therefore$ Total residue, $\frac{56x}{100}+\frac{40\,(1{\cdot}84-x)}{84}=0{\cdot}96$ gms

Whence $x=1$. $\therefore$ $CaCO_3 = 1$ gms, $MgCO_3 = 0{\cdot}84$ gms.

8. 16 gms. of pure MnO_2 are heated with excess of HCl and the gas evolved is passed into a solution of KI. Calculate the weight of iodine that is liberated.

(Mn = 55, Cl = 35·5, K = 39, I = 127).

Eqns. (i) $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$

$55+32=87 \qquad\qquad 71$

(ii) $Cl_2 + 2KI = 2KCl + I_2$

$71 \qquad\qquad 127\times 2 = 254$

87 gms MnO_2 produce 71 gms chlorine,

$\therefore$ 16 gms MnO_2 produce $\frac{71\times 16}{87}$ gm. chlorine.

But 71 gms chlorine liberates 254 gms. Iodine

$\therefore$ $\frac{71\times 16}{87}$ gms chlorine will liberate $\frac{254\times 71\times 16}{71\times 87}$ gm Iodine

That is 46·71 gms Iodine are liberated.

9. A quantity of a mixture KI and NaCl transformed into the normal sulphate (anhydrous) is found to weigh the same as the original salts. Find the composition of the mixture.

(K = 39, I = 127).

Let 1 gm. of the mixture contains x gm. NaCl. Then the weight of KI in the mixture is$(1-x)$ gm.

(i) $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$

$2(23+35{\cdot}5) \qquad 46+32+64$

$= 117 \qquad = 142$

(ii) $2KI + 2H_2SO_4 = K_2SO_4 + SO_2 + I_2 + 2H_2O$

$2(39+127) \qquad 78+32+64$

$= 332 \qquad = 174$

Then 117 gms NaCl produce 142 gms Na_2SO_4

$\therefore$ x gms NaCl will produce $\frac{142x}{117}$ gms Na_2SO_4.

and 332 gms. KI produce 174 gms. K_2SO_4

$\therefore$ $(1-x)$ gms KI will produce $\frac{174\,(1-x)}{332}$ gms K_2SO_4

By the given condition, $\frac{142x}{117} + \frac{174\,(1-x)}{332} = 1.$

$\therefore$ $x = {\cdot}6901 =$ wt. of NaCl.

$\therefore$ % of NaCl in the mixture = 69·01.

and % of KI in the mixture = 30·99.

In the foregoing calculations, the relative weights of reactants and products were used. But it is often more convenient to express the amounts in terms of moles instead of gram-weights. The following example will illustrate the mole method of cal-calculation.

Problem 10. How much $KClO_3$ must be strongly heated to yield as much oxgen as would be obtained from 200 gms. of mercuric oxide ?

Formula weight of $KClO_3 = 122{\cdot}5$; and that of $HgO = 216$,

$2HgO = 2Hg + O_2$; $2KClO_3 = 2KCl + 3O_2$.

Mole of $HgO = 200/216 = 0{\cdot}93$ moles.

1 mole HgO gives 0·5 mole of O_2.

$\therefore$ 0·93 moles of HgO will produce $0{\cdot}5 \times 0{\cdot}93 = 0{\cdot}465$ moles of oxygen.

Now 1 mole of oxygen is obtained from $\frac{2}{3}$ mole of $KClO_3$.

∴ 0·465 mole of oxygen is obtand from $\frac{2}{3}\times{}$·464 mole of $KClO_3$.

∴ the weight of $KClO_3$ required = $\frac{2}{3}\times{}$·465 × 122·5 = 37·98 gms.

Exercises—10.1

1. How much of the following substances would be required to produce 2·64 Kg of CO_2 ?

(i) $MgCO_3$, (ii) Carbon monoxide, (iii) ethyl alcohol.

[(i) 5·04, (ii) 1·68, (iii) 1·38 Kg].

2. What changes in weight will be observed on heating strongly one gram each of (i) $KClO_3$, (ii) $CaCO_3$.

[Decrease in weight ; (i) 0·392 gm, (ii) 0·44 gm].

3. How much Copper would dissolve in a silver nitrate solution when 0·24 gm silver is precipitated by it ? [0·07 gm].

4. Hydrogen, prepared by the action of sulphuric acid on 13 gm. of zinc. is passed separately over (i) 10 gms, (ii) 20 gms of dry and heated copper oxide. What will be the weight of the residue and its composition in each case ?

[(i) Residue Cu = 7·97 gm ; (ii) Residue, Cu (12·6 gm) + CuO (4·2 gm)]

5. How much hydrogen will be available by passing excess of steam over 112 gm of hot iron ? [5·4 gm.]

6. 0·2925 gm. of a speciman of common salt was dissolved in water and completely precipitated by a solution of $AgNO_3$. The precipitate after washing and drying was found to weigh 0·7075 gm. What was the percentage of sodium chloride in the specimen ? [Ag = 108, Cl = 35·5] [98·63 %],

7. Find out the ratio of the weights of $KClO_3$ and BaO_2 which would produce the same amount of oxygen ?

[K = 39, Ba = 137]. [1 : 414]

8. Find the minimum weight of iron required to produce 40 gms of hydrogen.

[840 gm Fe by steam-iron process].

9. What weight of zinc and sulphuric acid would be reqired to produce enough hydrogen to reduce completely 8·5 gms. of CuO to metallic copper ?

[Zn = 65·5, Cu = 63·5] [7 gm of Zn and 10·47 gms H_2SO_4]

10. 18 gms of water are decomposed completely by (i) sodium metal, (ii) electrolysis. Calculate the weight of hydrogen produced in each case.

[(i) 1 gm. (ii) 2 gms.].

11. How much H_2SO_4 is necessary to prepare 50 kg of $(NH_4)_2SO_4$? If the same H_2SO_4 is obtained from Pyrites (FeS_2), how much of the latter would be required ? [37·1 kg. 22·71 kg.]

12. 20 kg of nitric acid is prepared from chile salt petre, ($NaNO_3$) and 96% H_2SO_4. The saltpetre contained 92% $NaNO_3$. How much of this saltpetre and sulphuric acid would be necessary ?

[saltpetre = 29·3 kg, acid = 16·2 kg.]

13. 2·5 gm of a sample of $CaCO_3$ contained some silica as impurity. On strong heating the residue left weighed 1·62 gm. Find the purity of the sample of $CaCO_3$. [80% pure].

14. How much phosphorus must be burnt to remove all the oxygen present in 500 gm air? What would be the weight of the residual gas? Air contains 23% oxygen by weight. [P = 89·125 gm, N = 385 gm.]

15. What amount of calcium sulphate will be formed when 10 gm $CaCO_3$ is added to an equal amount of H_2SO_4? [13·6 gm.].

16. How much ammonia would be obtained by heating a mixture of 60 gm NH_4Cl and 40 gm CaO? [19·06 gm]

17. Exactly 2·06 gm of HNO_3 was required to dissolve 1 gm of an alloy of copper and silver. In what proportion the two metals were present in the alloy? [Cu = 63, Ag = 108] [Cu = 31·54% Ag = 68·46%]

18. 12·0 gm of a mixture of KCl and $KClO_3$ when strongly heated left a residue of 8·08 gm chloride. What was the percentage of chlorate in the mixture? [83·33%]

19. Three grams of a mixture of sodium carbonate and sodium bicarbonate lost 0·348 gm on heating. Calculate the percentage of sodium bicarbonate, in the mixture, [68·567%]

20. A solution of nitric acid of specific gravity 1·46 contains 60% HNO_3. What weight of this solution is theoretically required to dissolve 5 gm of CuO? [Cu = 63·5] [19·28 gm].

21. 1·4 gm of copper are displaced from a solution of copper sulphate in water by iron. Find the weight of iron sulphate produced. [Cu = 63·5. Fe = 56] [3·351 gm].

22. A sample of metallic zinc contains a little impurity which is inert to HCl. 10 gms of the sample of the metal react completely with 30·1 c.c. of HCl of sp. gr. 1·18. If this hydrochloric acid contains 30% HCl by weight, calculate the percentage of metal in the sample. (Zn = 65·4) (95·4%)

23. 5 gms of a mixture of copper oxide and copper powder were reduced in a stream of dry hydrogen, and the water formed was collected and weighed as 1·08 gms. What was the percentage of powdered copper in the mixture? (Cu = 63·5) [4·62%].

24. 15·25 gm of a mixture of $KClO_3$ and MnO_2 were heated and 4·8 gms of oxygen were liberated. What weight of MnO_2 was used as catalyst. [3 gms].

10·2. Problems on weight to volume relations :

From the chemical equations, the number of moles of the reactants and the products are known. If any one of the participants in the chemical change be gaseous, its volume would also be known, for, 1 mole of a gaseous substance occupies 22·4 litres at N.T.P. If, however, the pressure and temperature be different from N.T.P., then the gas equation PV/T = constant may be used to obtain the correct volume. Some illustrations are given here.

Problem 1. What weight of NH_4Cl would be required to prepare 10 litres of Ammonia at N. T. P. ?

$$\underset{2\times53\cdot9=107}{2NH_4Cl}+CaO=\underset{2\times22\cdot4\text{ litres.}}{2NH_3}+CaCl_2+H_2O$$

$2\times22\cdot4$ litres of NH_3 are produced from 107 gms NH_4Cl

$\therefore$ 10 litres of NH_3 are produced from $\dfrac{107\times10}{2\times22\cdot4}$

$$=23\cdot88 \text{ gms } NH_4Cl.$$

Problem 2. What volume of oxygen at 12°C and 780 gm. pressure would transform the hydrogen produced from 25 mm. zinc with excess hydrochloric acid into water ? (Zn = 65).

$$\underset{65}{Zn}+2HCl=ZnCl_2+\underset{22\cdot4\text{ litres at N. T. P.}}{H_2}$$

Now, 65 gms. Zn produce 22·4 litres of hydrogen at N. T. P.

$\therefore$ 25 gms Zn will produce $\dfrac{22\cdot4\times25}{65}$ litres of H_2 at N.T.P.

$$\underset{2\times22\cdot4\text{ litres}}{2H_2}+\underset{22\cdot4\text{ litres}}{O_2}=2H_2O$$

$2\times22\cdot4$ litres of Hydrogen react with 22·4 litres of oxygen at N.T.P.

$\therefore$ $\dfrac{22\cdot4\times25}{65}$ litres of H_2 will react with $\dfrac{22\cdot4\times22\cdot4\times25}{2\times22\cdot4\times65}$ litres of oxygen = 4·31 litres of oxygen at N.T.P.

Let v be the volume of oxygen at 12°C and 780 mm.

$$\therefore \frac{780 \times v}{285} = \frac{760 \times 4{\cdot}31}{273}$$

$$\therefore v = \frac{760 \times 4{\cdot}31 \times 285}{780 \times 273} \text{ litres.}$$

$$= 4{\cdot}38 \text{ litres.}$$

Problem 3. A baloon of 1000 litres capacity is to be fiilled with hydrogen at 30°C and 750 mm. pressure. What is the minimum quantity of iron required to liberate the necessary amount of hydrogen ?

Let 1000 litres of hydrogen at 30°C and 750 mm. occupy v litres at N. T. P.

$$\therefore \frac{1000 \times 750}{303} = \frac{v \times 760}{273} \text{ where } v = 889{\cdot}4 \text{ litres.}$$

(i) $3Fe + 4H_2O = Fe_3O_4 + 4H_2$

$3 \times 56 = 168$ gm. $\quad 4 \times 22{\cdot}4$ litres at N. T. P.

$4 \times 22{\cdot}4$ litres of H_2 are produced by 168 gms. Fe.

$$\therefore 889{\cdot}4 \text{ litres of } H_2 \text{ are produced by } \frac{168 \times 889{\cdot}4}{4 \times 22{\cdot}4} \text{ gm Fe}$$

$$= 1668 \text{ gm. of Iron.}$$

(ii) $Fe + H_2SO_4 = FeSO_4 + H_2$

1 mole hydrogen is liberated by 1 mole Fe

$$\therefore \frac{889{\cdot}4}{22{\cdot}4} \text{ moles of } H_2 \text{ will be liberated by } \frac{889{\cdot}4}{22{\cdot}4} \text{ moles of Fe}$$

$$\text{or, } \frac{889{\cdot}4}{22{\cdot}4} \times 56 = 2224 \text{ gm. of Fe.}$$

∴ the minimum quantity of iron required in steam-iron process = 1668 gm.

Problem 4. Air contains 23% of oxygen by weight. How many gram of sulphur will be required to burn out the oxygen in 100 litre of air at 30°c and 755 mm. pressure ?

Let 100 litres of air at 30°c and 755 mm. occupy v litres at N. T. P.

$\therefore \quad \frac{100 \times 755}{303} = \frac{v \times 760}{273}$ or, $v = 89{\cdot}5$ litres.

The weight of this volume of air at N. T. P. $= (89{\cdot}5 \times 14{\cdot}4 \times {\cdot}09)$ gm.

[$\because$ the density of air (relative to H) $= 14{\cdot}4$]. $= 116$ gms.

Now, 100 gm. air contain 23 gm. O_2

$\therefore$ 116 gm. air contain $\frac{23 \times 116}{100} = 26{\cdot}68$ gm. oxygen.

Again $S + O_2 = SO_2$

$\quad\;\; 32 \quad 32$

ie. 32 gm oxygen support the complete combustion of 32 gm. sulphur.

$\therefore$ 26·68 gm. oxygen will be burnt out by 26·68 gm. sulphur.

Problem 5. One gram of a sample of impure zinc when acted on by HCl produced 130 cc of hydrogen at 50°c and 755 mm. pressure. What was the percentage of pure zinc in the sample ? $(Zn = 65{\cdot}3)$.

Let v be the volume of the evolved hydrogen at N. T. P.

then $\frac{v \times 760}{273} = \frac{130 \times 755}{323}$, whence $v = 109{\cdot}1$ c.c.

$Zn \quad + 2HCl \quad = ZnCl_2 \quad + H_2$

65·3 gm. 22.4 litres at N. T. P.

$\therefore$ At N. T. P. 22400 cc. of hydrogen is produced by 65·3 gm. zinc.

$\therefore$ 109·1 cc of hydrogen is produced by $\frac{65{\cdot}3 \times 109{\cdot}1}{22400}$ gm. Zinc

$= 0{\cdot}3181$ gm. Zinc.

That is, 1 gm of sample contained 0·3181 gm. pure zinc.

or, the sample contains 31·81% pure zinc.

Problem 6. At 27°c and 750 mm pressure, a gas mixture contains 20% methane and 80% carbonmonoxide. 1·52 litres of this mixture was oxidised by oxygen produced by heating $KClO_3$. How much $KClO_3$ was used ? $(K = 39)$.

Let 1·52 litres of gas mixture occupy v litres N. T. P.

Then $\frac{v \times 760}{273} = \frac{1 \cdot 52 \times 750}{300}$, whence $v = 1 \cdot 365$ litres.

Eqn : $CH_4 \quad +2O_2 \quad = CO_2 \quad +2H_2O$

1 mole 2 moles

or 1 vol 2vols.

We have, at N.T.P., the vol. of $CH_4 = \frac{20 \times 1 \cdot 365}{100} = 0 \cdot 273$ litre.

and the volume of $CO = \frac{80 \times 1 \cdot 365}{100} = 1\ 092$ litres.

Now from the above equation, 0·273 litres of CH_4 would require for oxidation $2 \times 0 \cdot 273$ litres of oxygen.

Again, $2CO \quad +O_2 = 2CO_2$

2 vols. 1 vol.

Hence, 1·092 litres of CO would require for oxidation $\frac{1}{2} \times 1 \cdot 092$ litres of O_2.

Net requirement of $O_2 = 2 \times \cdot 273 + \frac{1}{2} \times 1 \cdot 092 = 1 \cdot 092$ litres at N. T. P.

$2KClO_3 \quad = 2KCl \quad +3O_2$

$2 \times 122 \cdot 9 \qquad 3 \times 22 \cdot 4$ litres (N. T. P.)

That is, 67·2 liters of O_2 is available from 245 gm. $KClO_3$.

$\therefore$ 1·092 litres of O_2 is available from $\frac{245 \times 1 \cdot 092}{67 \cdot 2}$

$= 3 \cdot 98$ gm. $KClO_3$.

Exercises—10-2

1. 100 gm. of KnO_3 are heated to redness, what volume of oxygen at 39°C and 765 mm. pressure is evolued ? (12·59 litres)

2. How many litres of CO_2 at 27° and 740 mm. pressure would be formed by burning acetylene (C_2H_2) derived from 96 gm CaC_2 ? [75·84 litres].

3. A mixture of Mg and Al weighing 1·50 gm. was completely dissolved in HCl and evolved 1·44 litres of hydrogen, measured at N.T.P. Calculate the weight of Mg in the mixture. [1·32 gm]

4. 20 gms each of copper and sulphur were separately boiled with conc. Sulphuric acid. What would be the ratio of volumes of sulphur dioxide produced in the two cases ? [32 : 184]

5. Air contains 21 % oxygen by volume. A variety of wax has the composition C = 80%, H = 20%. What volume of air at 27°C and 750 mm. would burn 60 gm of the wax ? [831·2 litres]

6. Ferric chloride obtained from 1 gm iron was dissolved in water. Calculate the volume of H_2S at N.T.P. which would completely reduce it to ferrous chloride. [200 c.c.]

7. One gm of a Sodium—amalgam on reaction with water gave 200 c.c. hydrogen at 13°C and normal pressure. What was the percentage of sodium in the amalgam ? [39·2 %]

8. One gm of a mixture of $CaCO_3$ and $MgCO_3$ when heated gave 240 c.c. CO_2 at N.T.P. Find out the proportion of the two components in the mixture [$MgCO_3$ = 37·88%]

9. Find out the volume of air at 91°C and 700 mm. pressure that would be required to burn completely one Kg. of coal containing 90 % carbon and 10 % non-combustible matter; Air contains 20 % oxygen by volume. [12160 litres]

10. H_2S, obtained by treating a sample of ferrous sulphide with dilute sulphuric acid contained 5 % of hydrogen by volume. What percentage of free iron did FeS contain ? [3·24 %]

11. A sample of 25 gms of pure chalk were uniformly mixed with pure silica ; 0·75 gms of the mixture when treated with hydrochloric acid liberated 125 c.c. of CO_2, measured at 27°C and 756 m.m. pressure. Find the amoun of silica that was mixed with the sample of chalk. [12·5 gm.]

12. What volume of chlorine, measured at 12°C and 780 m.m. pressure can be obtained when 110 gms of MnO_2 act upon corc. HCl. If the acid contains 38 % HCl and has a specific gravity of 1·2, what volume of it will be required ? (Mn = 55). [28·80 litres. 404·8 cc.]

13. Air contains 23 percent oxygen by weight. Its density (H = 1) is 14·4. What volume of air at N.T.P. is required to convert 1 gram of carbon into produce gas (CO and N_2) ? [4·478 l]

14. The weight of a solution of KOH increased by 0·08 gm when 100 litres air at N.T.P. was passed through it. What was the percentage of CO_2 in the air ? (0·0408 % by volume)

15' What weight of copper must be heated with conc. H_2SO_4 to produce 500 c.c. of SO_2 at 27°C and 750 mm. pressure ? What volume of H_2S at N.T.P. will be required to precipitate copper in the solution ? How much ferrous sulphide will give the requisite quantity of H_2S ? (Cu = 63·5, Fe = 56).

[1·2728 gms of copper, 0·4489 litres of H_2S, 1·76 gm FeS].

10.3. Problems on volume to Volume Relations (Eudiomtery) :—

Eudiometry refers to the study of the reactions involving gaseous substances by observing their volumes before and after the reaction. Such reactions are generally carried out in an eudiometer tube where volumes of gases can be measured. The instrument usually consists of a graduated tube closed at one end by a stop-cock and the gas under investigation is collected over a liquid, say mercury, in the tube. The volume can be read off directly under kuown conditions of tempreature and pressure.

When two or more gases are present in a mixture, the volumes of the individnal component can also be determined by absorbing a component by a suitable absorbent, viz, caustic potash for CO_2 and other acid gases, alkaline pyrogallate for oxygen, ammoniacal cuprous chloride for CO and acetylene, and so on.

The eudiometric calculations are mainly based on two relation ships derived from the Gay Lussac's Law of gaseous volumes and the Avogadro's hypothesis which has been discussed earlier. These are—(i) In gaseous reactions, the simple volume ratio of various reactants and the products is also the molar ratio and vice versa,

(ii) At N.T.P. the volume of any gas is 22·4 litres.

Thus, N_2	$+3H_2$	$=2NH_3$
1 gm. molecule	3 gm. molecules	2 gm. molecules
22·4 litres at NTP	3 × 22·4 litres at NTP	2 × 22·4 litres at NTP
1 vol.	3 vols	2 vols.

In eudiometric measurements the following facts should be remembered,—

(i) In gaseous reactions, the total volume may decrease, increase or remain the same ; as,

$2H_2 + O_2 = 2H_2O$ (steam)
2Vols 1 vol 2 vols ; contraction of 1 vol.
$H_2 + Cl_2 = 2HCl$; no change in volume
1 vol. 1 vol 2 vols
$CO_2 + C(s) = 2CO$; expansion of 1 vol.
1 vol 0 2 vols

(ii) The volume occupied by a liquid or solid is negligibly small compared with that of a gas ; they are, therefore, supposed to occupy zero volume in eudiometry.

(iii) In comparing the volumes of the gases involved in a reaction, 1 gm-molecule of any gas is assumed to occupy 1 volume. In all othor cases, the actual volume, viz. 22·4 litres at N.T.P. is always taken.

(iv) Whenever hydrogen and oxygen combine together to produce steam, which on cooling condenses to water occupying negligible volume. there is thus a contraction in volume. One-third of the contraction will represent the volume of oxygen and two-thirds of the contraction will represent the volume of hydrogen taking part in the reaction.

The various types of problems on Eudiometry may be classified as follous—

(a) Volume to volume relationship in simple gaseous reactions.

(b) Determination of composition of gas mixture.

(c) Determination of molecular formulla of gases and gaseous hydrocarbons.

(*a*) *Problems on simple gaseous reactions.*

Problem 1. What volume of carbon monoxide at N.T.P. will be available from 100 litres of carbondioxide passed over red-hot coke ?

$$CO_2 + C = 2CO$$

1 vol 2 vols.

1 litre of CO_2 will produce 2 liters of CO.

∴ 100 litres of CO_2 will poduce 200 litres of CO.

Problem 2. What volume of oxygen would be required for the complete combustion of 250 cc each of the following gases ;

(a) ethylene, (b) methane ?

(a) $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$

1 vol 3vols

1 litre of C_2H_4 will require 3 litres of O_2 for complete combustion.

∴ 250 cc of C_2H_4 will require $3 \times \frac{1}{4}$ litre or 750 cc of O_2 for complete combustion.

(b) $CH_4 + 2O_2 = CO_2 + 2H_2O$
1 vol 2 vols

1 litre CH_4 will require 2 litres of O_2 for complete combustion.

∴ 250 cc CH_4 will reqnire $2 \times \frac{1}{4}$ or 500 cc of O_2 for complete combustion.

Problem 3. 100 cc of carbon monoxide are mixed with 40 c.c. of oxygen and exploded. If the resulting mixture is shaken with caustic potash, what volume of the gas will remain and what gas will it be ?

$2CO + O_2 = 2CO_2$
2 vols 1 vol 2 vols

Hence 40 c.c. oxygen must combine with 80 c.c. carbon monoxide to produce 80 c.c. of CO_2.

So, the volume of unchanged CO-gas $= 100 - 80 = 20$ cc and the gas-mixture after explosion contains CO $= 20$ cc; $CO_2 = 80$ cc

Now, on being shaken with KOH, this 80 cc CO_2 is absorbed.

Hence there remains only 20 cc carbon monoxide gas.

Problem 4. What volume of chlorine at N.T.P. would be required to (i) combine with 10 litres of ethylene ; (ii) decompose 10 litres of H_2S ?

(i) $C_2H_4 + Cl_2 = C_2H_4Cl_2$
1 vol 1 vol

It is seen that 1 vol ethylene requires 1 vol. of chlorine for complete reaction.

∴ for 10 litres of ethylene, 10 litres of chlorine will be required.

(ii) $H_2S + Cl_2 = S + 2HCl$
1 vol 1 vol

1 vol. chlorine is required for complete oxidation of 1 vol. H_2S.

∴ 10 litres of H_2S will be oxidised by 10 litres of chlorine.

Problem 5. Air contains 21% oxygen, 79%N_2. The oxygen present was fully used up by red hot carbon into 'producer gas', what is the composition of the producer gas ?

In 100 cc of air, the vol of oxygen = 21 cc and vol of N_2 = 79 cc.

$2C + O_2 = 2CO.$
1 vol 2 vols.

∴ 21 cc. of O_2 give rise to 42 cc. CO.

∴ tne producer gas contains 42 cc CO and 79 cc N_2. Total vol = 121 cc.

$$\therefore \% \text{ of } CO = \frac{42 \times 100}{121} = 34{\cdot}7.$$

$$\% \text{ of } N_2 = \frac{79 \times 100}{121} = 65{\cdot}3.$$

(*b*) *Problems on composition of gas mixtures.*

Problem 6. When 150 cc of ozonised oxygen were passed through a red-hot tube, 160 cc. of gas remained. calculate the compoition of the original mixture.

$2O_3 = 3O_2$
2 vols 3 vols.

Suppose 150 cc. of the gas contained x cc. of ozone.
Now 2 cc. of ozone yields 3 cc. of oxygen.
∴ x cc of ozone yields $\frac{3}{2} \times x$ cc of oxygen.
So. the volume after the change, $(150 - x) + \frac{3}{2}x = 160$
or, $x = 20$ cc.

∴ 150 cc of ozonised oxygen contatined 20 cc ozone.

$$\therefore \% \text{ of ozone in ozonised oxygen} = \frac{20 \times 100}{150} = 13{\cdot}33.$$

Problem 7. 50 cc. of a mixture of CO and CO_2 were mixed with 15 cc oxygen and the mixture was exploded in an eudiometer. After shaking with KOH solution, 5 cc of oxygen where left. Find the composition of the gaseous mixture.

Let the mixture contains x cc CO. ∴ vol. of $CO_2 = (50 - x)$ cc with oxygen only CO will react producing CO_2. Since 5 cc oxygen was left unreacted, only (15-5) = 10 cc of oxygen reacted.

Now, $2CO + O_2 = 2CO_2$
2 vols 1 vol 2 vols.

1 vol. oxygen is required for 2 vols CO.

$\therefore$ 10 cc. oxygen were required for 20 cc. CO.

Hence the mixture contains 20 cc CO and $(50-20)=30$ cc. CO_2.

Problem 8. When 60 cc of a mixture of N_2O and NO were mixed with equal volume of pure hydrogen and exploded, 38 cc of pure N_2 were left. Calculate the quantity of each gas in the original mixture.

Let x cc be the volume of N_2O, $\therefore$ $(60-x)$ cc = volume of NO.

$N_2O \quad + \quad H_2 \quad = \quad H_2O \quad + \quad N_2$
1 vol 1 vol (water) 1 vol

$2NO \quad + \quad 2H_2 \quad = \quad 2H_2O \quad + \quad N_2$
2vols 2 vols = (water) 1 vol.

1 vol. N_2O gives on explosion 1 vol of nitrogen.

$\therefore$ x cc. N_2O will give on explosion with hydrogen, x cc of N_2.

Again, 2 vols of NO, give on explosion 1 vol of nitrogen.

$\therefore$ $(60-x)$ cc of NO will given $\left(\frac{60-x}{2}\right)$cc of Nitrogen.

But the total volume of nitrogen produced = 38 cc.

Hence, $x+\frac{60-x}{2}=38$ or $x=16$ cc

Thus the composition of mixture is $N_2O=16$ cc, $NO=44$ cc.

Problem 9. 10 cc of a mixture of CO, CH_4 and Nitrogen, exploded with excess of oxygen, gave a contraction of 6·5 cc ; there was a further contraction of 7 cc. when the residual gas was treated with KOH. What was the composition of the original mixture ?

Let x cc. be the volume of CO, and y cc be the volume of CH_4.

$\therefore$ vol of $N_2=(10-\overline{x+y})$ cc

The effect of the explosion is

(a) $2CO \quad + O_2 \quad = 2CO_2$
2 vols 1vol 2vols $\therefore$ contraction = 1vol.

(b) $CH_4 \quad + 2O_2 \quad = CO_2 + 2H_2O$
1vol 2vols 1 vol (liquid) $\therefore$ contraction = 2vols.

from (a) : Contraction = half the vol of CO = $\frac{x}{2}$.

from (b) : Contraction = double the vol of $CH_4 = 2y$.

$\therefore \ \frac{x}{2}+2y=6{\cdot}5$ or, $x+4y=13$ ....(i)

Again, the second contraction of 7 cc., after treatment with KOH solution, must be due to formation of CO_2.

Now fron (a) : vol of CO_2 formed = vol of $CO = x$.

from (b) : vol of CO_2 formed = vol of $CH_4 = y$.

$\therefore \ x+y=7$ ....(ii)

Solving (i) and (ii), we have $x=5$, $y=2$:

Hence : the composition of original mixture is $\begin{cases} CO = 5 \text{ cc} \\ CH_4 = 2 \text{ cc} \\ N_2 = 3 \text{ cc} \end{cases}$

Problem 10. A sample of coal gas contains 40% H_2, 35% CH_4, 15% CO and 10% C_2H_2 ; 100 cc of this gas were exploded with 600 c.c. of air (containing 21% O_2 by volume) in a eudiometer. Calculate the composition of the resulting mixture on cooling.

600 cc air contains $21 \times 6 = 126$ cc O_2, $\therefore$ Vol of $N_2 = 474$ c.c.

Now,

$$\begin{array}{llll} 2H_2 & + \ O_2 & = 2H_2O\ (l) & \\ 40 \text{ cc} & 20 \text{ cc} & & \\ CH_4 & +2O_2 & =CO_2+H_2O\ (l) & \\ 35 \text{ cc} & 70 \text{ cc} & 35 \text{ cc} & \\ 2CO & +O_2 & =2CO_2 & \\ 15 \text{ cc} & 7{\cdot}5 \text{ cc} & 15 \text{ cc} & \\ 2C_2H_2 & +5O_2 & =4CO_2+2H_2O(l) & \\ 10 \text{ cc} & 25 \text{ cc} & 20 \text{ cc} & \end{array}$$

Therefore,

Vol of O_2 used up

$= (20+70+7{\cdot}5+25)$ cc

$= 122{\cdot}5$ cc

So Vol of O_2 left unreacted

$= 126-122{\cdot}5 = 3{\cdot}5$ cc

Vol of CO_2 formed

$= (35+15+20) = 70$ cc

So the composition of the resulting mixture :—

$N_2 = 474$ cc ; $O_2 = 3{\cdot}5$ cc $CO_2 = 70$ cc

$$\text{i.e., } \left.\begin{array}{l} N_2 = \dfrac{474 \times 100}{574{\cdot}5} = 86{\cdot}58\% \\ O_2 = \dfrac{3{\cdot}5 \times 100}{547{\cdot}5} = 0{\cdot}64\% \\ CO_2 = \dfrac{70 \times 100}{547{\cdot}5} = 12{\cdot}78\% \end{array}\right\}$$

(c) *Problems on the molecular formula of gases and gaseous hydrocarbons.*

It has been discussed earlier that the knowledge of volumes of gaseous substances participating in a chemical change enables us to determine the composition of molecular formula of a compound using Avogadro's hypothesis. The following examples will explain the method.

Problem 11. At N.T.P. 30 cc of nitrogen peroxide when passed over heated copper yield 15 cc of nitrogen. The vapour density of the oxide is found to be 23. What is the molecular formula of the oxide ?

$$\underset{30\text{ cc}}{\text{Nitrogen peroxide}} + Cu \longrightarrow \underset{15\text{ cc}}{N_2} + CuO$$

So, 30 cc of nitrogen peroxide yield 15 cc of Nitrogen. That is, nitrogen peroxide contains half its volume of nitrogen or, 1 cc Nitrogen peroxide contains $\frac{1}{2}$ c.c. Nitrogen. From Avogadro's hypothesis.

1 molecule of nitrogen peroxide contains $\frac{1}{2}$ molecule or 1 atom of nitrogen ($\because$ N_2 molecule is diatomic)

Hence the molecular formula of nitrogen peroxide may be represented as NO_x. $\therefore$ Molecular wt. $= 14 + 16x$.

Again Mol. wt. $= 2 \times$ vap. density $= 2 \times 23 = 46$.

$\therefore\ 14 + 16x = 46$ or, $x = 2$

Therefore, the formula of nitrogen peroxide is NO_2.

Problem 12. 10 cc of nitrous oxide are mixed with electrolytic gas and sparked. On cooling, the volume becomes 15 cc. After adding alkaline pyrogallate, the volume of the residual gas (Nitrogen) is found to be 10 cc. Deduce the formula of nitrous oxide.

$$\text{nitrous oxide} + \underset{(O_2)}{H_2} \rightarrow H_2O\,(l) + \underset{(O_2)}{N_2}.$$

Electrolytic gas contains hydrogen and oxygen in the ratio of 2 : 1 by volume.

Now, After 1st. explosion, on cooling the volume = 15 cc and the vol. of the residual gas after adding alkaline pyrogallate = 10 cc. which is only due to nitrogen.

∴ 10 cc of nitrous oxide yield 10 cc nitrogen.

∴ Oxygen left unreacted $= 15 - 10 = 5$ cc which must come from electrolytic gas.

∴ the electrolytic gas contains 10 cc Hydrogen, which will react with 5 cc oxygen to produce water and this 5 cc oxygen must be present in 10 cc nitrous oxide.

∴ 10 cc nitrous oxide contain 10 cc nitrogen and 5 cc oxygen.

From Avogadro's hypothesis—1 molecule nitrous oxide contain 1 molecule nitrogen and $\frac{1}{2}$ molecule oxygen.

Or, 1 molecule nitrous oxide contains 2 atoms of nitrogen and 1 atom of oxygen.

∴ the molecular formula of nitrous oxide is N_2O.

Molecular formula of gaseous hydrocarbons :

The formula of a gaseous hydrocarbon is often determined by exploding a known volume of the gas with excess of oxygen in a eudiometer tube. On explosion, the hydrocarbon produces CO_2 and H_2O and it is accompanied with a contraction in volume. This contraction is measured. A second contraction observed when KOH is introduced into the system which absorbs CO_2. This contraction which gives the volume of CO_2 produced is also measured. The residual gas is unused oxygen. Measurements are made at ordinary temperature and hence the volume of $H_2O(l)$ is always ignored. The principle of calculation may be explained as follows :—

Contraction on explosion = (volume of gases before explosion)
(1st contraction) − (volume of gases after explosion)

∴ 1st. contraction = (vol. of hydrocarbon + vol. of oxygen taken) − (vol of CO_2 formed + vol of O_2 left unused)

or, 1st. contraction (ie. contraction on explosion)
= vol. of hydrocarbon + (vol. of O_2 taken − vol. of O_2 left unused) − vol, CO_2 formed.

or, contraction on explosion = vol of hydrocarbon + vol. of oxygen actually used up − vol CO_2 formed.

∴ vol. of oxygen used up = contraction on explosion (1st contraction) + vol. of CO_2 formed (2nd contraction) − vol. of hydrocarbon.

Now, the volume of oxygen used up for burning the carbon = vol. of CO_2 formed.

Hence the volume of oxygen required for hydrogen = total vol of oxygen used − vol of CO_2 formed.

From the known volume of the hydrocarbon taken and the two contractions, the formula of the hydrocarbon can be easily established.

Problem : *13.* 20 cc of a gaseous hydrocarbon are exploded with excess of oxygen, The contraction observed was 30 cc. There was a further contraction of 40 cc on treatment with KOH. What is the molecular formula of the hydrocarbon ?

We know,

vol of oxygen used up = 1st. contraction + 2nd contraction − vol. of hydrocrbon.

or, vol of oxygen used up = 30 cc. + 40 cc − 20c = 50 cc.

vol of caıbondioxide formed = 2nd contraction = 40 cc.

Now the formation of 40cc CO_2 required 40 cc O_2 out of the 50 cc. O_2 used up.

Hence, H_2O must have been formed from 10 cc. oxygen. And 10 cc O_2 obviously required 20 cc H_2 which was derived from the hydrocarbon.

So, 20 cc. hydrocarbon contain 20 cc. H_2 and give 40 cc. CO_2.

or, *n* molecules of hydrocarbon contain *n* molecules of Hydrogen and provide 2*n* molecules of CO_2.

or, 1 molecule hydrocarbon contains 1 molecule hydrogen and gives 2 molecules of CO_2.

Now, 2 molecules CO_2 = 2 atoms of carbon ; 1 molecule hydrogen = 2 atoms of hydrogen.

Hence the molecular formula of the hydrocarbon is C_2H_2.

Alternately, Let the formula of the hydrocarbon be C_xH_y, where, *x* and *y* stand for atoms of carbon and hydrogen respectively. The equation for the reaction which occurs on explosion is :

$$C_xH_y+\left(x+\frac{y}{4}\right)O_2=xCO_2+\frac{y}{2}H_2O\ (l).$$

$$1\ \text{vol.}\quad \left(x+\frac{y}{4}\right)\text{vol}\quad x\ \text{vol}\quad 0\ \text{vol.}$$

$$\text{or,}\quad 20\ \text{cc}\quad 20\left(x+\frac{y}{4}\right)\text{cc}\quad 20x\ \text{cc}\quad 0\ \text{cc}$$

Hence contraction on explosion : $20+20\left(x+\frac{y}{4}\right)-20x=30$ cc

The CO_2 formed is $20x=40$ cc

Solving $x=2$, $y=2$.

Hence the formula of the hydrocarbon is C_2H_2.

The farmula of the gaseous hydrocarbon can also be determined when the volume of oxygen added is not known, only the 1st. contraction and the density of the hydrocarbon are known. The principle of calculation may be explained as follow :—

We have seen that,

vol of hydrocarbon + vol. of oxygen used up = 1st. contraction + 2nd contraction.

Now, the vol of oxygen used up = vol of oxygen combined with hydrogen of the hydrocarbon + vol of oxygen combined with carbon of the hydrocarbon.

Since the 2nd contraction is due to the formation of CO_2 and as CO_2 contains its own volume of oxygen, the vol. of oxygen combined with carbon = 2nd cantraction.

Therefore, vol of hydrocarbon + vol of oxygen combined with hydrogen = 1st. contraction.

∴ the vol of oxygen combined with hydrogen of the hydrocarbon = 1st. contraction − vol of hydrocarbon.

∴ the vol. of hydrogen present in the hydrocarbon is twice this volume.

Problem 14. 20 cc of a gaseous hydrocarbon are exploded with oxygen avoiding excess. On cooling, the volume contracts by 60 cc. The density of hydrocarbon is 22. Find the formula.

Here the volume of oxygen combined with hydrogen only $= 60 - 20 = 40$ cc. This will react with 80 cc of hydrogen which are present in 20 cc of the hydrocarbon.

That is, 20 cc hydrocarbon contain 80 cc hydrogen.

or, 1 cc hydrocarbon contains 4 cc. hydrogen.

or, 1 molecule hydrocarbon contains 4 molecules i.e., 8 atoms of hydrogen.

$\therefore$ The molecular formula may be represent as C_xH_8.

So, its mol. wt. $= 12x + 8$.

But the mol. wt. of the hydrocarbon $= 2 \times 22 = 44$.

That is, $12x + 8 = 44$. $\therefore x = 3$.

Hence the formula is C_3H_8.

Exercises—10-3

1. What volume of oxygen at N.T.P. is required to effect complete combustion of 100 c.c. of ethylene ? [300 c.c.]

2. 70 c.c. of CO are mixed with 28 c.c. of oxygen and exploded. If the resulting mixture is shaken with caustic potash, what volume of gas will remain and what gas will it be ? [14 c.c., CO]

3. Air contains 20% oxygen by volume. What volume of air will be needed to produce 1000 litres of SO_2 by burning sulphur ? [5000 litres]

4. Estimate the volume of hydrogen necessary to produce 50 litres ammonia at the same temperature and pressure. [75 litres]

5. Assuming air to contain 21% oxygen by volume, what volume of air at 27°C and 755 mm. will be required for the complete combustion of one litre of each of the following gases at the same temperature and pressure ? (a) Hydrogen ; (b) Methane ; (c) Carbon monoxide.
[(a) 2·38 litres : (b) 9·52 litres, (c) 2·38 litres]

6. When 75 c.c. of ozonised oxygen was passed through a red-hot tube, the volume expanded to 80 c.c. What was the percentage of ozone in the gas ? [13·33%]

7. To a mixture of an unknown nitrogen oxide and 30 c.c. nitrous oxide was added 60 c.c. hydrogen and exploded. On cooling, the final volume was found to be 45 c.c. of nitrogen only. The unknown nitrogen oxide is 15 times as heavy as hydrogen. Find the formula of the unknown oxide. [NO]

8. 25 cc. of oxygen was subjected to silent electric discharge when the volume was reduced to 20 cc. What would be the proportion of ozone in the ozonised oxygen ? [50%]

9. 20 cc. methane was mixed with 100 cc. oxygen and electrically sparked. What will be the volume after sparking (neglect volume of liquid water) and what gases would be present then ? [80 cc. ; O_2 and CO_2]

10 What volume of air at 27°C and 750 mm. would be required for the complete combustion of 100 cc. of a gaseous mixture containing 46% H_2 ; 40% marsh gas ; and 14% CO by volume? Air contains 79% N_2 and 21% oxygen by volume. [583·2 c.c.]

11. A sample of coal-gas has the composition $H_2=45\%$, $CH_4=30\%$; $CO=20\%$ and $C_2H_2=5\%$. 100 cc. of this coal gas was mixed with 160 cc. of oxygen and exploded. What gases would remain after explosion and in what volumes ? [$CO_2=60$ cc. ; $O_2=55$ cc.]

12. 10 cc. of a mixture of CO_2, CH_4 and C_2H_4 exploded with excess of oxygen, gave a contraction of 17 cc. ; there was a further contraction of 14 cc. when the residual gas was treated with KOH. What was the composition of the gas mixture ? [$CO_2=1{\cdot}5$ cc. $CH_4=4{\cdot}5$ cc. $C_2H_4=4$ cc.]

13. 50 cc. of a mixture of chlorine monoxide (Cl_2O) and chlorine dioxide (ClO_2) was decomposed by careful heating. The chlorine produced was absorbed by KOH and the volume decreased by 40 cc. Calculate the composition of the original gaseous mixture. [$Cl_2O=30$ cc. ; $ClO_2=20$ cc.]

14. The gaseous product evolved on heating a mixture of oxalic acid and formic acid and Conc. H_2SO_4, is led into caustic potash solution when the volume is decreased by one-sixth. Calculate the molar ratio of the organic acids in the mixture. [1:4]

15. 100 cc. of a mixture of N_2O and NO are slowly passed over red hot copper. The resulting gas occupied a volume of 85 cc., both measured under the same condition ; 20 cc. of Oxygen were added to another 100 cc. of the same mixture and the volume contracted in this case from 120 cc. to 105 cc. Assuming that the NO is converted into NO_2, find the composition of this 105 cc. of gas mixture. [70 cc. N_2O + 30 cc. NO_2 + 5 cc. O_2.]

16. Find the composition of ammonia from the following data :—vol. of ammonia taken = 22·5 cc ; volume after sparking for sometime = 45 cc. ; volume after addition of oxygen = 188·5 cc., volume after explosion = 137·88 cc. [NH_3]

17. Find the composition of the nitrous oxide from the following date :—
(a) vol. of gas taken = 10 cc. , (b) vol. after addition of hydrogen = 28 cc.
(c) vol. after explosion = 18 cc. (d) vol. after addition of oxygen = 27 cc.
(e) vol. after second explosion = 15 cc. [no H_2 remains after 2nd explosion].
[N_2O]

18. 8 cc. nitric oxide were heated with a spiral of iron by means of electric current. On cooling, the volume of the gas left was found to be 4 cc. at the original temp. and pressure. 136·8 cc. of nitric oxide at N. T. P. weigh 0·18 gm. Deduce the formula of nitric oxide from the data. [NO]

19. To oxidise 20 cc. of a mixture, of methane, ethylene and acetylene 49 cc. of O_2 was required and 33 cc. of CO_2 was produced. Find the composition of the gas mixture. ($CH_4=7$ cc. ; $C_2H_4=5$ cc. ; $C_2H_2=8$ cc.)

20. 20 cc. of a hydrocarbon was mixed with 80 cc. oxygen and exploded. The volume after explosion was 60 cc. It was then shaken with KOH solution and the volume was reduced to 20 cc. What is the formula of the hydrocarbon ? [C_2H_4]

21. 20 c. c. of a hydrocarbon was mixed with 250 c. c. air and exploded. A contraction in volume of 40 c.c. was noticed. On absorption with KOH, the volume of CO_2 produce was found to be 20 cc. What is the formula of the hydrocarbon ? [CH_4]

22. 10 cc. cf a gaseous hydrocarbon are exploded with 100 cc. of oxygen. The residual gas, on cooling, is found to measure 95 cc., of which 20 c.c. are absorbed by caustic soda and the remainder by alkaline pyrogallol. Determine the formula of the hydrocarbon. [C_2H_2]

23. 12 cc. of a gaseous hydrocarbon when exploded with excess of oxygen underwent a contraction of 24 c. c. and on being treated with KOH, a further contraction of 12 c. c. occured. What was the hydrocarbon ? [CH_4]

24. 10 cc. of a hydrocarbon (vap. density = 28) was exploded with excess of oxygen when a contraction of 30 cc. occured. What is its formula ? [C_4H_8]

25. 1 litre of a 3:2 mixture of water gas ($H_2$50, CO47, $CO_2$3) and producer gas ($N_2$60, CO35, $CO_2$5) is mixed with excess steam and passed over an ironoxide catalyst. Find the nitrogen—hydrogen ratio in the resulting gases. [1:3].

ON FORMULAE

It has already been discussed that the percentage compostion of a compound can be determined from the formula. When the formula of a compound is given, the molecular weight of the substance is known from the atomic weights. Hence, the gm. atoms of the constituent atoms in a gm-molecule of the substance is also known. From this the percentage of the constituent elements in the compound, i.e. its percentage composition can be determined. For example :

Problem 1. Find out the percentage composition of Epsom salt.

The molecular formula of Epsom salt is $MgSO_4, 7H_2O$.

wt. of 1 atom of magnesium $= 1 \times 24 = 24$
wt. of 1 atom of sulphur $= 1 \times 32 = 32$
wt. of 4 atoms of oxygen $= 4 \times 16 = 64$
wt. of 7 molecules water $= 7 \times 18 = 126$

$\therefore$ formula weight of $MgSO_4, 7H_2O = 246$

Therefore, 1 gm. mole Epsom salt, i.e., 246 gm. of $MgSO_4, 7H_2O$ contains 24 gms of Mg, 32 gm. of S, 64 gm of O_2 and 126 gm of water of crystallisation.

That is, percentage of $Mg = (24/246) \times 100 = 9{\cdot}76\%$
percentage of $S = (32/246) \times 100 = 13{\cdot}01\%$
percentage $O_2 = (54/246) = 100 - 26{\cdot}01\%$
percentage of $H_2O = (126/246) \times 100 = 51{\cdot}22\%$

In this section we shall discuss how the formula of the compound can be deduced from its percentage composition, i.e., the reverse of the above calculation.

10.4. To determine the formula from percentage composition :—

If the percentages of the constituent elements of a compound be known from analysis, the results would give up the empirical formula of the compound, which simply indicates the relative number of atoms of each elements present in the compound. The principle of calculation may be explained as follows ;—

Suppose a compound is formed from $x\%$ of the element A and $y\%$ of the element B. Let the formula of the compound is A_pB_q, where p, q the number of atoms of A and B respectively are unknown simple integers.

Let a and b stand for the atomic weights of the two elements.

If the molecular weight of the substance be M then

$$\text{the percentage of } A = \frac{pa \times 100}{M} = x$$

$$\text{and the percentage of } B = \frac{qb \times 100}{M} = y$$

$$\therefore \quad \frac{pa}{qb} = \frac{x}{y}\,; \text{ i.e. } \frac{p}{q} = \frac{x/a}{y/b}.$$

$$\text{Hence } p : q = \frac{x}{a} : \frac{y}{b} = \frac{\%\text{ of } A}{\text{At.wt. of } A} : \frac{\%\text{ of } B}{\text{At. wt. of } B}.$$

Since the quantities on the right side are known, the ratio of the number of atoms ($p : q$) is known, though the exact values of p and q are not known. Thus the empirical formula of the compound can be obtained. Hence to derive the simple or empirical formula of compound from the percentage composition, the following steps of calculations should be followed :

(1) The percentages of the constituent atoms should be divided by the respective atomic weights in each case. The ratio of these quotients lead to the empirical formula.

(2) The ratio, if fractional, should be transformed into integral ratio by dividing the quotients by the smallest of them. This is necessary as atoms are present in integral numbers and cannot be fractional.

(3) If the ratio thus obtained are still not of whole numbers, the quotients are further multiplied by a common number to make them all integral.

The above procedure gives the empirical formula of the compound. This cannot provide us with the exact number of atoms of each element in a molecule, i.e., the molecular formula of the compound cannot be ascertained. The molecular formula is either equal to or simple multiple of the empirical formula. The two formulae are related to each other as :

Molecular formula = (Empirical formula)$_n$,
where n is a simple integer.

Thus when $n=1$, the two formulae are the same, otherwise not. It follows from the above relation that,

$$n=\frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

Therefore the value of n can be easily obtained if the molecular weight of compound be separately determined. The molecular formula is then calculated by multiplying the empirical formula by the value of n thus obtained.

Illustrations :

Problem 2. A salt has the following prcentage compostion : Na = 37·38, H = 1·11, C = 14·29, O = 57·40. Find its simplest formula.

The weight ratio of constituent elements :

$Na : H : C : O = 27{\cdot}38 : 1{\cdot}19 : 14{\cdot}29 : 57{\cdot}40$

The ratio of their number of atoms would be obtained by dividing each with their respective atomic weights.

$$Na : H : C : O = \frac{27{\cdot}38}{23} : \frac{1{\cdot}19}{1} : \frac{14{\cdot}29}{12} : \frac{57{\cdot}40}{16}$$

$$1{\cdot}19 : 1{\cdot}19 : 1{\cdot}19 : 3{\cdot}58$$

In order to make this ratio an integral one, each has to be divided by the smallest of them,

$$Na : H : C : O = \frac{1{\cdot}19}{1{\cdot}19} : \frac{1{\cdot}19}{1{\cdot}19} : \frac{1{\cdot}19}{1{\cdot}19} : \frac{3{\cdot}58}{1{\cdot}19}$$

$$1 : 1 : 1 : 3$$

∴ the simplest (empirical) formula required is $NaHCO_3$.

Problem : 3 A colourless crystalline compound has the following percentage composition : Sulphur 24·24%, Nitrogen 21·21%, Hydrogen 6·06%, the rest is Oxygen. Determine the empirical formula of the compound. Give the name of the compound, if the molecular formula be the same as the empirical formula and if it is found to be a sulphate.

S = 24·24%, N = 21·21%, H = 6·06%, ∴ O = 100 − 51·51 = 48·49%

Hence, the weight ratio, S : N : H : O = 24·24 : 21·21 : 6·06 : 48·49.

Dividing each with their respective atomic weight,

$$\text{Ratio of atoms, } S : N : H : O = \frac{24{\cdot}24}{32} : \frac{21{\cdot}21}{14} : \frac{6{\cdot}06}{1} : \frac{48{\cdot}49}{16}$$

$$= 0{\cdot}757 : 1{\cdot}515 : 6{\cdot}06 : 3{\cdot}03$$

Now, dividing each number by the lowest number 0·757, we have, S : N : H : O = 1 : 2 : 8 : 4.

∴ the empirical formula of the compound is $SN_2H_8O_4$.

Since the empirical formula and the molecular formula of the substance are the same, and the compound is a sulphate, the molecular formula of the compound is $N_2H_8(SO_4)$ or, $(NH_4)_2\ SO_4$.

∴ the name of the compound is ammonium sulphate.

Problem 4. A compound formed from sulphur, chlorine and oxygen contains S = 23·76% and Cl = 52·54%. Its vapour density is 67·75. Suggest its molecular formula.

S = 23·76%, Cl = 52·54%, ∴ O = 100 − 76·30 = 23·70%

Hence the weight ratio, S : O : Cl = 23·76 : 23·70 : 52·54.

$$\therefore \text{ Ratio of atoms, } S : O : Cl = \frac{23{\cdot}76}{32} : \frac{23{\cdot}70}{16} : \frac{52{\cdot}54}{35{\cdot}5}$$

(dividing each with respective at wts)

$$= 0{\cdot}74 : 1{\cdot}48 : 1{\cdot}48$$

= 1 : 2 : 2 (Dividing each by the lowest number 0·74)

∴ the empirical formula of the compound is SO_2Cl_2. So its molecular formula will be $(SO_2Cl_2)_n$.

Now, the vap. density of the compound = 67·75.

∴ its molecular weight = 67·75 × 2 = 135·50.

Therefore $(32 + 32 + 71)n = 135{\cdot}5$

or, $135n = 135{\cdot}5$ ∴ $n \approx 1$. (∵ n must be an integer).

∴ the molecular formula of the compound is SO_2Cl_2.

Problem 5. A compound contains 37·8% carbon, 6·3% hydrogen and 55·9% chlorine. 0·638 gm. of the compound when vaporised occupies a volume of 154 cc. at 100°c and normal pressure. What is the molecular formula of the compound ?

The ratio of the wts C : H : Cl = 37·8 : 6.3 : 55·9

$$\therefore \text{ the ratio of the atoms } C : H : Cl = \frac{37\cdot8}{12} : \frac{6\cdot3}{1} : \frac{55\cdot9}{35\cdot5}$$

$$= 3\cdot15 : 6\cdot30 : 1\cdot570$$

$$= 2 : 4 : 1 \text{ (dividing each by } 1\cdot575).$$

Hence the empirical formula of the compound = C_2H_4Cl.

$\therefore$ the molecular formula will be $(C_2H_4Cl)_n$

Let *M* be the molecular weight of the compound. From the given data, we have,

$$PV = \frac{w}{M}RT \text{ or, } M = \frac{wRT}{PV}$$

$$\therefore M = \frac{0\cdot638 \times \cdot082 \times 373}{1 \times 0\cdot154}$$

$$= 126\cdot7$$

$\because$ $w = 0\cdot638$ gm.

$P = 1$ atom.

$V = 154$ cc $= 0\cdot154$ lit.

$R = \cdot082$ lit. atm.

$T = 373°A$

Hence, $(2 \times 12 + 4 \times 1 + 35\cdot5) \times n = 126\cdot7$

or, $63\cdot5\, n = 126\cdot7$ $\therefore n \approx 2$ (taking nearest whole number)

$\therefore$ the molecular formula = $C_4H_8Cl_2$.

Problem 6. Barium chloride crystals ($BaCl_2xH_2O$) contains 14·73% water of crystallisation. Find out the complete formula of these crystals. (Ba = 137'4, Cl = 35·5)

The Mol. wt. of $BaCl_2 = 137\cdot4 + 2 \times 35\cdot5 = 208\cdot4$

The Mol. wt. of water = 18.

In the crystals, water = 14·73%, hence $BaCl_2 = 100 - 14\cdot73$ 85·27%

The weight ratio ; $BaCl_2 : H_2O = 85\cdot27 : 14\cdot73$

$$\text{The ratio of the molecules ; } BaCl_2 : H_2O = \frac{85\cdot27}{208\cdot4} : \frac{14\cdot73}{18}$$

$$= 0\cdot409 : 0\cdot818 = 1 : 2$$

Since there is one $BaCl_2$ molecule, so the number of H_2O molecules would be 2.

So, the required formula is $BaCl_2, 2H_2O$.

Exercises—10·4

1. Find out the percentage of the metal present in ferric oxide [Fe_2O_3] and in red lead (Pb_4O_4). [Fe=56, Pb=208] [Fe=70% , Pb=90·65%]

2. On analysis, a mixture of cuprous and cupric oxide [$Cu_2O + CuO$] was found to have Cu=88%. In what proportion the two oxides are present? [Cu=63·5] [Cu_2O=91·01%]

3. A molecule of sulphur dioxide contains one atom of sulphur and two atoms of oxygen. The compound contain 50% of sulphur by weight. What is the ratio of atomic weights of sulphur and oxygen ?

[at. wt. of S. : at. wt. of O=2 : 1]

(Other exercises on percentage composition are given in chapter)

4. Water contains 11·11% hydrogen. Establish its formula. [H_2O]

5. A certain iron sulphide contains 46·6% Fe and 53·4%S. Calculate its empirical formula. [Fe=56] [FeS_2]

6. 1 gm of a compound contains 0·262 gm nitrogen, 0·075 gm hydrogen and 0·663 gm chloride. Find its simplest formula. [NH_4Cl]

7. A substance has the following composition N=35%, H=5%, O=60% On heating it yields a gas containing N=63·63% and O=36·37%. Determine the formula of each substance. [NH_4NO_3, N_2O]

8. A compound containing Na, S, O and H gave on analysis the following result : Na=14·31%, S=9·97%, H=6·25%, O=69·47%. Calculate the formula on the assumption that all the hydrogen in the compound is present in combination with oxygen as water. [$Na_2SO_4, 10\,H_2O$]

9. Two oxides of a metal contain 27·6 and 30% oxygen respectively. If the formula of the first oxide be M_3O_4, find that of the Second. [M_2O_3]

10. Acetic acid contains 40% carbon and 53·33% oxygen. The rest is hydrogen. Its molecular weight is 60% Find out its molecular formula.

[$C_2H_4O_2$]

11. A compound of carbon, hydrogen and oxygen contains C 40%, H 6·67. When the compound is vaporised, its vapour density is fouud to be 2·813 times than that of oxygen. Find the empirical and molecular formula of the compound ? [CH_2O , $C_3H_6O_3$]

12. A gaseous hydrocarbon 14·59% Hydrogen, 46·43 cc. of the gas at 11 cc. and 749 mm., weigh 0·11gm. What is its molecular formula ? [C_4H_8]

13. Two compounds are formed from carbon, hydrogen and oxygen. Their percentage composition and vapour densities are given, Find out their formulae.

(a) C 54·54 H=9·09%, O=36·37% ... vap. density=132.

(b) C 38·7%, H=9·68%, O=51·61% ... vap. density=31

[$C_{12}H_{24}O_6$, $C_2H_6O_2$]

14. A hydrated solid when heated loses moisture and the weight decreases by 45·6%. The anhydrous substance, on analysis is found to have the composition, Al=10·5%, K 15·1%, S=24·8%, O=49·6%

Find out the formulae of both anhydrous and the hydrated compound.

(Al=27, K=39, S=33) [$KAlS_2O_8$, $KAlS_2O_8$, $12H_2O$]

15. Chloroform is a compound of Carbon, hydrogen and chlorine. Its composition is C=10·04%, Cl=89·12%. The vapour density of chloroform is 59·75. Find out its molecular formula. [$CHCl_3$

16. Anhydrous megnesium sulphate is $MgSO_4$. The hydrate crystal contains 51·22% water. What will be the formula of the hydrated magnesium sulphate. (Mg=24, S=32) [Mg SO, $7H_2O$]

17. A crystalline salt contains 18·55% sodium, 25·71% sulphur, 19,35% oxygen (which is not present as water) and 36·29% water of crystallisation. What is its formula ? [$Na_2S_2O_3$, $5H_2O$]

18. Find the formula from the following percentage composition :

$MgO=23·48\%$, $FeO=41·74\%$, $SiO_2=34·78\%$

[Mg=24, Fe=56, Si=28] [MgO, Fe*O*, SiO_2 or Mg $FeSiO_4$]

19. A substance gives on analysis the following results :

Na=13·4%, Sb=23·3%, S=24·9%, and H_2O38·4%. It contains 7% hygroscopic moisture. Calculate the formula of the compound, (Na=23, Sb=120, S=32). [Na_3SbS_4, $9H_2O$]

[Hint : Since the compound contains 7% hygroscopic miosture, the % of water of crystallisation is 38·4—7=31·4, and the actual wt. of the compound is (100−7)=93. Now calculate the percentage composition of the pure substance and from this percentage composition determine the formula].

20. One gram of a gaseous hydrocarbon gives on combustion 2·93 gm. of CO_2 and 1.8 gm of H_2O. One litre of the hydrocarbon at N. T. P. weighs 0·134 gm. Find out the molecular formula of the hydrocarbon [C_2H_6]

21. A monobasic organic acid contains 6·66% H, 39·96% C and the rest oxygen, 0·167 gm of the silver salt of the acid gave 0·108 gm of silver on ignition, Find the formula of the acid. (Ag=108) [$C_2H_4O_2$]

22. In an experiment to determine the composition by weight of carbon dioxide, it was found that 0·66 gms. of carbon dioxide were obtained from 0·18 gms. of carbon. From this result, show how the formula of the gas may be deduced.

CHAPTER—XI

SOLUTIONS & SOLUBILITY : CRYSTALLISATION : COLLOIDS

The subject of solutions is one of great interest and importance. Many natural phenomena are dircetly concerned with solution. It is through the media of solutions that the plant distributes the mineral matter from the roots to the leaves. It is through the same medium that food enters living organisms. According to Ostwald, almost all the chemical processes which occur in nature take place between substances in solution.

11-1. Solutions : When a small quantity of sugar is added to a glass of water and stirred, the sugar disappears in water giving a homogeneous mixture. Sugar distributes itself uniformly throughout the mass of the liquid. Though the sugar is not observable even under the most powerful microscope, the taste of the solution would reveal its existence. Such a homogeneous mixture of two or more non-reacting substances, where the components are inseparable by any physical boundary and the composition remains uniform all throughout the mixture, is called a solution. The sugar is said to be dissolved in water to form the solution. Similar phenomena occur when urea, copper-sulphate, common salt, soda, glucose, etc., are added to water. These substances are *soluble* in water. But if chalk or sand or sulphur be added to water, they will not dissolve in water. They will settle at the bottom, for, these substances are *insoluble* in water.

The solution, however, cannot be classed as a compound, for it is possible to vary the composition of this "mixture" within certain limits, by the addition of some more sugar or water. We may, therefore, state that,

A solution is a homogeneous mixture of two or more substances, whose composition may be varied within certain limits. In a solution the different substances are uniformly and intimately mixed with each other in a state of molecular dispersion, which has, therefore, the same composition and physical properties in every part.

Solute and solvent : The terms *solute* and *solvent* refer to the components of the solution. It is obvious that a solution must consist of at least two substances (i.e., binary solution)—the substance which has dissolved and that which dissolved it. The dissolved substance is called the *solute*, and the dissolving medium, in which the solute are unifomly dispersed through dissolution. known as the *solvent*. It may therefore, be written as :

Solution = Solute + Solvent.

It may be mentioned that in a solution it is sometimes difficult to differentiate between the solute and the solvent. Usually the component, which is present in greater amount relative to the other and which is in the same physical state as the solution, is called the solvent—while the component in smaller amount is called the solute. For instance, when a solution is made by dissolving a solid substance (e.g , salt. sugar etc.) in a liquid, where the liquid is present in large excess over the solid, there is no ambiguity in these terms, the solid being the *solute* and the liquid the *solvent*. But in a solution where the components are in the same physical state (say, a solution of alcohol in water), if the quantity of water is more, it is the solvent and alcohol the solute ; if the quantity of alcohol is more, it is the solvent and water the solute. The rectified spirit contains 96% alcohol and 4% water approximately, so alcohol is the solvent and water is the solute. However, solute and solvent are terms of convenience and should not be used when they might lead to ambiguity. In the case of a 50% alcohol and water solution, it would be better to avoid the terms solute and solvent.

11-2. Types of Solutions :—

Depending upon the state of the solute and that of the solvent, the following types of solutions are possible.

1. *Solution of Gases in Gases* :—All gases mix homogeneously in all proportions and according to definition, the gas-mixtures are solutions. Examples : air, electrolytic gas, etc.

2. *Solution of Gases in liquids* :—Liquids can also dissolve gases. Examples :—Aerated water, such as soda water, contains carbondioxide gas dissolved in water under pressure. Ordinary water also contains air dissolved in it.

3. *Solution of Gases in Solids* : Example : Hydrogen dissolved (occluded) in palladium or platinum.

4. *Solution of Liquids in Liquids* :—Some liquids dissolve each other. Examples : A mixture of alcohol and .water, a mixture of benzene and xylene etc.

5. *Solution of Liquids in Solids* :—Example : liquid metallic mercurry is dissolved by some metals such as gold, silver, sodium etc. to form amalgams.

6. *Solution of Solids in Liquids* :—This is the usual types of solutions. Examples :—Solution of common salt or sugar in water, solution of iodine in alcohol etc.

7. *Solution of Solids in Solids* :—Many solids dissolve, in the molten state, some other solids, which on cooling produce solid solutions. Examples : various alloys. such as brass, bronze, etc.

Of these types, the solutions of solids in liquid are the usual types of solutions and are of immense importance to the chemists. We shall limit our discussion in this chapter to such solutions.

Water is the most common solvent widely used. It dissolves various types of substances. Liquids other than water may also act as solvents e.g., alcohol, ether, benzene, carbondisulphide, acetone, etc. Thus, sulphur is soluble in carbondisulphide, oils and fats in benzene, iodine in chloroform etc. Alcoholic solutions of medicines are called tinctures e.g. tincture of iodine. It is not possible to predict whether a given solid will dissolve in a liquid and, if so, upto what extent, but it is generally observed that the substances which are alike chemically can mutually dissolve in each other giving rise to solutions. Thus non-polar (covalent) compounds dssolve in non-associated (non-polar) solvents such as carbon tetra-chloride, benzene, chloroform etc., but insoluble in polar solvents like water, and that polar compounds (ionic) dissolve in associated (polar) liquids such as water, liquid ammonia etc., but are insoluble in non-polar solvents. For instance, sodium chloride is a polar (ionic) compound and so, it easily disssolves in polar solvent water, but insoluble in benzene, which is a non-polar solvent.

Solutions are mixtures and not chemical compounds

Like a compound, a solution is homogeneous and there is no surface of separation between the components, bnt the solution is a mixture and differs from chemical compound in several respects.

(1) The individual properties of both solute and solvent are retained. So a solution is a mixture not a compound.

(2) Solute can be separated from the solvent by easy physical means like distillation, crystallisation etc. It would not be possible if solute was chemically combined with the solvent.

(3) The relative proportions of the components of a solution can be varied within a limited range, which is not possible in a chemical compound.

(4) The properties of solutions, such as, boiling point, freezing point and vapour pressure, vary with the concentration of the solution, whereas compounds have fixed and definite physical properties.

11.3. Concentration of solution : Saturated, Unsaturated and Super-saturated solutions.

The proportion of solute and solvent in a given solution is an important quantity. The concentration of a solution is the quntity of the solute cantained in a definite weight or in a definite volume of the solution. When the solution contains a relatively small amount of solute, it is called a *dilute solution.* If the relative amount of solute is large, the solution is said to be *concentrated.* It is obvious that concentrated solutions are possible only when the solute is very soluble.

The concentration of the solution may bc expressed as :

(i) number of grams of solute, (a) in 100 grams of solution i.e., the percentage by weight of solute, (b) in 100 grams of solvent ; (c) in 1 litre of solution.

(ii) number of gram-molecules of solute , (a) in 1000 grams of solvent (molality). (b) in 1 litre of solution. (molarity).

A solution which contains 1 gram-molecule of solute in 1000 grams of solvent is *1 molal solution* and a solution which contains 1 gram-molecule of solute in 1 litre of solution is *1 molar solution.*

Now, there is limit to the amount of the solid that may dissolve in a given quantity of a liquid at a particular temperature. When, for example, potassium nitrate (nitre) is added in successive small amounts to some quantity of water taken in a beaker and stirred at a fixed temperature, it dissolves in water upto a certain extent only ; after this the nitre no longer passes into solution but simply settles out unchanged at the bottom of the beaker. This means that the given amount of solvent has dissolved the maximum quantity of the solute possible at that temperature. Any further addition of nitre will not change the composition of the solution. and a solution which is in equilibrium with the excess undissolved solute results. Such a solution is said to be saturated with the solute and is called a *saturated solution.* A condition of equilibrium, thus, exists between the dissolved and the solid states of the solute :

$$\underset{\text{(dissolved)}}{\text{Solute}} \rightleftharpoons \underset{\text{(solid)}}{\text{Solute.}}$$

This state of saturation or equilibrium may be disturbed either by adding more water to or raising the temperature of the solution. A solution saturated at one temperature may not be saturated at another temperature. so a saturated solution without mentioning of its temp. is meaningless.

Hence, *a saturated solution is one which contains the maximum amount of the solute the given quantity of the solvent can possibly dissolve at a given temperature in presence of excess of solute.*

When the amount of solute present in a given solution is less than that required to saturate the same at the temperature, it is called an *unsaturated solution.* An unsaturated solution, therefore, dissolves more of the solute when brought in contact with it.

Sometimes, it is possible to make a solution, which under certain conditions, contains more solute than what is neccssary for its saturation at the same temperature. Such a solution is called a *super-saturated solution* which is metastable. Vigorous shaking or addition of a minute crystal of the solute would cause immediate separation of the excess solute. Thus—

A super saturated solution is one which contains more dissolved solute than is required to saturate the given quantity of the solvent at the same temperature.

From the above discussions, it is clear that if the concentration of a solution remains unchanged in contact with the solute at a particular temperature, the solution is said to be saturated in respect of the solute at that temperature. If the concentration increases in contact with the solute, it is unsaturated ; while if the concentration falls in contact with the solute, it is supersaturated.

N.B. A solution can never be super-saturated in contact with the solute.

Test of saturated, unsaturated and super-saturated solutions :

In order to test whether a solution of a substance (solid in water) is saturated. unsaturated or super-saturated at a particular temperature, it is only required to introduce a small crystal of the solute into the solution.

(i) if the solution is saturated, the added solute will not dissolve and the concentration of the solution will not change.

(ii) if the solution is unsaturated, the added solute will dissolve, either partially or completely, and thereby the concentration of the solution will increase.

(iii) if the solution is super-saturated, the added crystal will grow in size and the concentration of the solution will fall.

Prepartion of a super-saturated solution.

The tendency for super saturation depends primarily on the nature of the solute. Sodium sulphate, sodium acetate, sodium thiosulphate, alum etc. can form easily super saturated solutions. Liquid honey is a super saturated solution of sugar mainly.

A super-saturated solution of sodium thiosulphate, $Na_2S_2O_3$, $5H_2O$, also called hypo, is prepared by simply heating the solid substance in a lage test-tube. Hypo contains combined water known as the water of crystallisation and on heating it dissolves in this water. The mouth of the test tube is plugged with a piece of cotton wool to prevent entry of dust particles. On cooling carefully, this remains as liquid and no hypo is deposited. A super-saturated solution of hypo is thus formed. If now a minute crystal of the thiosulphate is added, immediately the whole mass would become solid with evolution of heat.

11.4. Mechanism of the Dissolution Process :

When a small quantity of solid (solute) is added to a given amount of liquid (solvent) at a definite temperature, there is an interaction between the solvent molecules and the solute particles (molecules in case of nonpolar solutes or ions in case of electrolytes). Through such solute-solvent interaction, the solvent molecules can exert sufficient force to tear off the solute particles from the surface of the solid, which then diffuse freely throughout the solvent giving a uniform solution. The process of dissolution continues until a dynamic equilibrium between the undissolved solid and solid in solution is established, and a saturated solution results. At this stage, in a given time a certain number of solute particles leave the solution and coalesce with the solid crystals, and an equal number of particles fall off the crystals and pass into the solution. A saturated solution at a given temperature is thus a solution which is in equilibrium with undissolved solid.

11.5. Solubility :

Solubility of a substance is its capacity to dissolve in a given solvent. Substances differ greatly in the extent to which they dissolve in water, for example, sugar is more soluble in water than common salt. The measure of the solubility of a substance is the concentration of its saturated solution and so it is expressed as follows :—

The solubility of a substauce (i.e. solute) in a solvent at a given temperature is the number of grams of the solute which dissolves in 100 grams of the solvent to give a saturated solution at that temperature. Thus, at 20°C, 100 gm. water dissolves 36 gm of common salt to form a saturated solution. The solubility of common salt in water at 20°C is thus 36·0. Similarly the solubility of potassium nitrate is 110 at 60°C means that 100 gms of water will dissolve 110 gm of potassium nitrate at 60°C to yield a saturated solution at the said temperature.

Hence, solubility (at a particular temperature)

$$= \frac{\text{weight of solute in gms}}{\text{weight of solvent in gms}} \times 100$$

If 'a' gm of a solute saturate 'b' gm of a solvent at t°C, then its solubility at t°C = 100a/b.

But, if x gms of a solute be present in y gms of its saturated solution at t°C, then its solubility at t°C $= \frac{100x}{y-x}$. The solubilities of a few salts at 100°C in water are given below :

Table : Solubilities in water at 100°c (gm/100 gm)

Solute	—	NaCl	KCl	KNO_3	Na_2SO_4	$Pb(NO_3)_2$	$KClO_3$
Solubility	—	39·2	60	246	42	138·8	57

N. B. The solubility is commonly expressed in gms per 100 gms of solvent at a specified temperature. However, in practice the numerical value is only used to indicate the solubility as it is seen from the above formula, the solubility of a substance is a number.

11.6. Factors influencing solubility :

(1) Solubility depends much upon the chemical nature of the solute and of the solvent. It is observed that different solid substances possess different solubilities in the same solvent and under the same condition of temperature. For example, 100 gms

of water at 50°C can hold in solution a maximum amount of 85·5 grams of potassium nitrate or 80·2 grm of potassium bromide or 36·67 gms of sodium chloride i. e, they posses different solubilities. Again, it is observed that the same solid substance shows different solubilites in different solvents. Common salt, for example, is soluble in water but not in alcohol. No generalisation can be made in this regard. The rate of dissolution, however, may be hastened by increasing the surface area of solid by powdering or by mechanical agitation of the mixture of the solute and the solvent by stiring or shaking.

(ii) The solubility of a substance is greatly influened by temperature, and so solubility without mention of temperature is meaningless. The solubility of a solid generally increases with the rise of temperature, but for different solids it may not increase to the same extent. In certain cases the solubility may also decrease with temperature. This will be discussed shortly in details. The solubility of liquids in liquids also has been found to rise with temperature, but the solubility of gases in solids or liquids generally decreases with increase of temperature.

(iii) Pressure has very little effect on the solubility of solids in liquids or of liquids in liquids. But pressure influences the solution of gases in liquids profoundly. With increase of pressure, the solibility of a gas increases, According to Henry's law, *the mass of a gas*(m) *dissolved by a unit volume of a liquid is proportional to the pressure* (p) *of the gas at constant temperature*, i, e., $\frac{m}{p} =$ constant. If the pressure be lowered the disolved gas will escape from the solution. This is why when soda-water bottle is opened the gas immediately comes out.

1.7 . Determination of Solubility :

The solubility of a solid in a liquid can be very easily determined in the laboratory. The procedure involves two steps :

(i) the preparation of a saturated solution,

(ii) the estimation of the weights of solid and liquid present in the saturated solution.

The determination of the solubilities of sodium chloride in water at room temperature illustrates the principle of the method.

Experiment : Some sodium chloride crystals are grounded in a mortar, and agitated with a quantity of distilled water taken in a glass-stoppered clean bottle for about 1 hour till some of the salt remains undissolved. Thus a saturated solution of common salt in water at room temperature is prepared. It is then altowed to stand for sometime.

Now a small evaporating basin made of thin glass is cleaned, dried and weighed in a chemical balance. A few ml. of the saturated solution, prepared above, is then filtered in the evaporating basin through a dry filter paper. The basin with the solution is then weighed carefully, so that the amount of the solution taken is known. The basin is then heated on a water-bath until the entire amount of water of the solution evoporates off and solid sodium chloride is left behind in the dish (Fig 11.1)—care must be taken to avoid loss of salt by spirting. The basin with the solid residue in it is then dried in an air oven (100°C), cooled in a desicator and weighed again. The processes of heating, cooling and weighing are repeated till the final weight is constant. This will ensure complete removal of water. The solubility is then calculated as follows :

Fig. 11.1.
water bath

Suppose, —(i) the weight of the dry empty basin $= a$ gm;

(ii) the weight of the basin + salt solution $= b$ gm.

(iii) the weight of the basin + salt left after evaporation $= c$ gm.

(iv) the temperature of the room $= t°$C.

∴ the weight of sodium chloride which was dissolved $= (c - a)$ gm.

and the weight of water which dissolved this amount of salt $= (b - c)$ gm.

That is $(c-a)$ gm of water dissolve $(b-c)$ gm of Sodium choloride to give a saturated solution of the room temp t°C.

or, 100 gm water dissolve $\frac{(c-a)}{(b-c)} \times 100$ gms of sodium chloride.

$\therefore$ the solubility of Sodium choloride at room temperature

$$= \frac{(c-a)}{(b-c)} \times 100.$$

When the solubilities of a solid in a liquid at different temperatures are required, the experiment is done in a thermostat using a modified arrangement of the apparatus as described below.

Experiment : To determine the solubility of nitre (potassium nitrate) at different temperatures, a wide-mouthed hard glass test-tube half filled with distilled water is taken. Sufficient quantity of powdered nitre in excess is added to water so that the solution would be saturated. The test tube is fitted with a rubber-cork, through which a thermometer, a stirrer and a pipette are introduced as shown in Fig 11-2. The whole thing is placed in a large thermostat whose temperature may be controlled as required. The stirrer helps in the process of saturation, the thermometer records the temperature. The saturated solution is kept for sufficient time at the desired temperature. Then about 5 c. c. of the saturated solution is pipetted off and transferred to a previously weighed evaporating basin. The mouth of the pipette is tied with a filter paper so that no solid could enter the pipette. The basin is then dried and the weight of the solute and water determined exactly as in the previous experiment. By adjusting the temperature of the thermostat solubilities at different temperatures, both higher or lower than the room temparature, can be obtained. The following table shows the

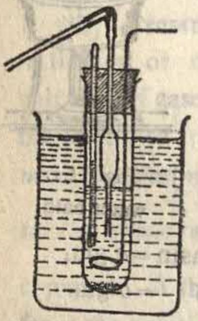


Fig. 11.2. Solubility determination at diff. temperature

solubilities of nitre in water at different temperatures as obtained by the above experiment.

Temperature (°C) ..	0°	10°	20°	40°	60°	80°	100°
Solubility···	13·4	20·9	32	64	110	169	247

11 8. Solubility Curves :

It has already been stated that the solubility of a substance is greatly influenced by the change of temparature. So temperature is always mentioned to express the solubility of a substance The change of solubility of a solid with temperature is most easily recorded graphically by plotting the solubility along the ordinate and the temperature along the abscissa and so obtaining a curve, known as the *solubility curve* for the solid.

Hence, the curve, obtained by plotting solubilities of a given substance in a given solvent at different temperatures which shows the influence of temperature on the solubility of the substance, is called the solubility curve for the substbnce.

The figures 11-3 and 11-4 give a number of solubility curves for various substances at temperatures ranging from 0° to 100°C, In order to draw such curves, the solubility of each of the salts has been determined at different temperatures by the method discussed earlier. The solubilities and the corresponding temperatures are then plotted along Y axis and X axis respectively. The points thus obtained are joined by smooth curve and the corresponding solubility curve is thus drawn.

Characteristics of the curves :

An examination of these curves would reveal the following facts :

(i) It is seen from Fig. 11.3. that the solubility of a solid in a liquid generally increases with the rise of temperature, but the solubility curves of different salts are different in type. This indicates that the rate of charge of solubilities of different salts with temperature is different.

(*a*) The solubility curves for silver nitrate, potassium nitrate, sodium nitrate and lead nitrate are very steep indicating that the solubilities of these salts increase rapidly with the rise of temp.

(*b*) The solubility curves for ammonium chloride, potassium chloride, potassium chlorare, mercuric chloride and potassium bromide are not so much steep, this shows that their solubilities, no doubt rises, but do not change so rapidly as those for the substances mentioned in (a).

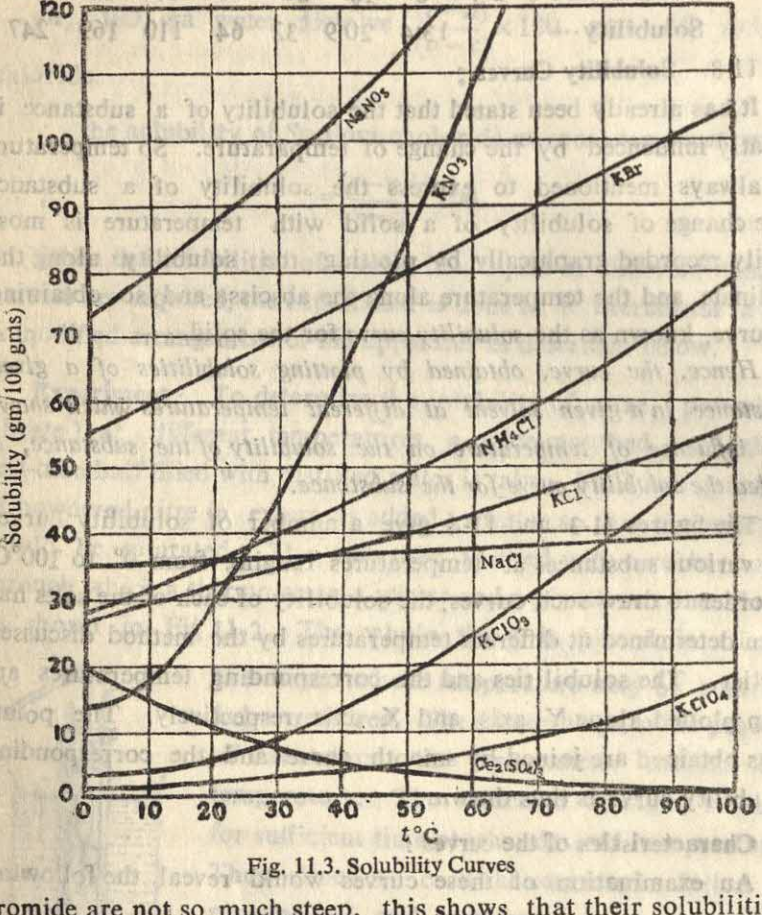


Fig. 11.3. Solubility Curves

(*c*) Sodium chloride shows almost a horizontal solubility curve i.e., it is almost parallel to the temperature axis. This indicates that sodium chloride is hardly more soluble in hot water than in cold.

(2) There are few exceptions where the solubility decreases with increase of temperature ; such as in the case of calcium

hydroxide, calcium acatate, cerous sulphate in water. These compounds are more soluble in cold water than in hot water. In these cases, the solubility curves slope downwards.

In both the above types, the solubility curves are continuous. For those solutes where solubility increases with temperature, the process of dissolution of the solute is accompanied with absorption of heat, i.e., the process is endothermic. This is indeed predicted from Le chatelier's principle. In case of solute whose solubility decreases with temp, the process is exothermic,

(3) There are instances where discontinuity in solubility cnrve is observed e.g., sodium sulphate, ferrous, sulphate, calcium chloride, sodium carbonate etc. (Fig 11.4.) This discontinuity is always due to the change in the composition of the solute salt. The solubility of sodium sulphate in water increases rapidly upto 32·4°C and then falls gently. Thus the curves for sodium sulphate shows a sharp break at 32·4°C, at which the decahydrate Na_2SO_4, $10H_2O$ changes to anhydrous salt Na_2SO_4. Such solubility curves are really made up of separate solubility curves for the different substances, i.e., Na_2SO_4, $10H_2O$ and Na_2SO_4 respectively. The former shows a rise in solubility and the latter shows a fall in solubility with temperature, these two separate curves intersect at temperature 32·4°C, Hence sodium sulphate has the maximum solubility at 32·4°C. In ferric chloride, calcium chloride, and other

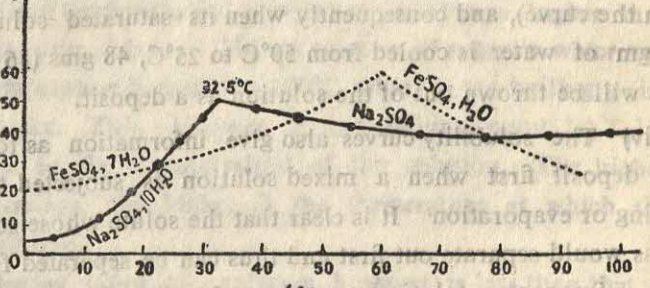


Fig. 11.4. Discontinuity in Solubility curves

solutions there occur more than one breaks in the solubility curves. At the breaking point, one hydrate passes to another hydrate or to the anhydrous salt. Every system has its fixed break, called the transition point. Thus 32·4°C is the transition temperature between the decahydrate and the anhydrous Na_2SO_4.

Utility of solubility curves :

The solubility curves are very useful because these curves provide us with the following important informations.

(i) The solubility of a substance at a given temperature can be directly read out from its solubility curve, also a comparative idea of the solubilities of different substances at a particular temperature may easily be made with the help of their solubility curves. For example, it is found from the solubility curves that the solubilities of different substances at a particular temperature. say 50°C, decreases in the following order :

$NaNO_3 > KNO_3 > Pb(NO_3)_2 > NH_4Cl > KCl > NaCl > KClO_3$ etc.

(ii) A clear idea of the change in the solubility of substances with change of temperature can be derived from the shape of the solubility curve. The steeper the curve the greater is the change, the flatter the curve, the slower is the change.

(iii) The solubility curve also tells us how much solid would be thrown out of solution, when its saturated solution at a higher temperature is cooled down to a lower temperature. For example, the solubility of nitre at 50°C is 86 and at 25°C it is 38 (as found from the curve), and consequently when its saturated solution in 100 gm of water is cooled from 50°C to 25°C, 48 gms (86—38) of nitre will be thrown out of the solution as a deposit.

(iv) The solubility curves also give information as to which will deposit first when a mixed solution is subjected to either cooling or evaporation· It is clear that the solute whose solubility is less would separate out first and thus can be separated from the other. Suppose a solution contains 40 gm each of potassium nitrate and potassium chlorate in 100 gm water at 100°C. On cooling, $KClO_3$ would separate out first when the temparature comes down to 70°C. This is because $KClO_3$ is less soluble than

KNO_3 and it requires 32 gm of the salt to keep the solution saturated. So (40−32)=8 gm of $KClO_3$ would separate out. But KNO_3 being more soluble and 40 gm of the salt is much less than the amount required for its saturated solution (i.e. 130 gm) at this temp. KNO_3 will remain in solution. If the temparature is further lowered to say 20°C, the solid which would separate would contain 10 gm KNO_3 and 35 gm $KClO_3$. Because from the solubility curve, we find the solubility of KNO_3 is 30 and that of $KClO_3$ is 5 at 20°C. Likewise, if the same mixture is subjected to evaporation, the curves tell us that the solution gets saturated with $KClO_3$ first, as its solubility is less than that of KCl. Hence, $KClO_3$ will be deposited first and until the solution also gets saturated with KCl.

This principle is the basis of separation of two soluble solids by fractional crystallisation. provided their solubilities differ widely. This will be discussed shortly.

11-9. Boiling point and freezing point of solntions :

A pure liquid has a fixed boiling point and freezing point which are always measured under normal atmospheric pressure. Thus water boils at 100°C and freezes at 0°C under one atomospheric pressure. But when a solute is added to a liquid these boiling and freezing temperatures are no longer fixed. That is, the boiling point and freezing points of solutions are differnt from those of pure solvent.

The boiling temperature of a solution is always higher than that of the pure solvent. Thus a solution of sugar in water will boil at a temperature higher than 100°C, which is the boiling point of pure water. This increase in the boiling point (ΔT_b) is proportional to the concentration of the solution. The higher the concentration, the higher is the temperature at which the solution will boil.

The freezing point of a solution, however, is less than that of the pure solvent. So the sugar solution will freeze at a temperature lower than 0°C, which is the normal freezing point of pure water. This decrease in the freezing point (ΔT_f) is also proportional to the concentraion of the solution. The greater the concentration, the lower is the freezing point.

When common salt is added to a mixture of ice and water (at 0°C), the salt dissolves and the freezing point is lowered, the ice therefore melts. If sufficient salt is added, the temperature goes to as low a temperature as −21°C when the solution would freeze. This mixture has a very low temperature and is called "freezing mixture", extensively used in the laboratory and also for preservation of meat, fish etc. The temperature of a freezing mixture of ice and calcium chloride in the ratio 1 : 2 falls to −55°C.

11-10. Crystallisation : Crystals.

It has been observed that when a saturated solution of a solid in a suitable liquid, prepared at a higher temperature, is allowed to cool down, some of the dissolved solid is thrown out of the solution. These are deposited in the form of particles having regular and definite geometrical forms. Such deposited solids are called crystals and the process is known as crystallisation. Hence—

Crystals are homogeneous solids, bounded by perfectly plane faces meeting in sharp edges and possossing regular and definite geometical form which they spontaeously acquire during their formation.

Crystalline and amorphous solids :—Substances in the solid state are either *crystalline* or *amorphous* (non crystalline). Most simple chemical substances in the solid state are *crystalline*. Diamond, graphite, alum, common salt, sugar, sulphur, ice, urea, blue vitriol and various other pure solids appear in crystalline forms. All crystals of the same substance have the same geometrical shape although they can be of different sizes : Common salt (cubic), graphite (hexagonal), alum (octahedral), sulphur (monoclinic), etc. Some of the crystal forms are shown in Fig 11-5. From x-ray analysis, it is known that the geometrical shape of a crystal is an expression of the orderly arrangement of the structural units (namely, atoms, ions or molecules) of the crystal. This arrangement is constantly repeated in all directions as the crystal grows.

Besides the definite shape there are other characteristics of crystals ; (i) The angles between corresponding faces of all the crystals of a given substance are constant and are characteristic of the substance,

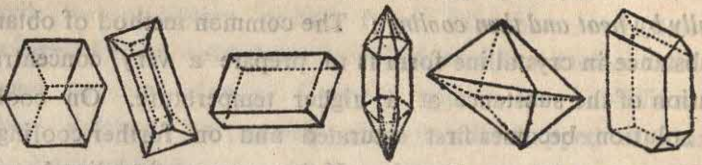


Fig. 11.5. Different forms of crystals

(ii) A crystalline solid has a sharp melting point, and

(iii) A crystal when given a sudden blow would very often break along some planes parallel to some crystal faces. These. planes along which crystals easily break up are known as 'cleavage planes'. Mica has one marked cleavage plane and it easily splits into sheets.

Amorphous solids have no definite crystalline form. Pitch, glass, lime, gelatine etc. are examples of amorphous solids. When they are subjected to pressure, they break up into irregular bits and do not cleave along any particular plane. Besides, such solids do not melt sharply at a fixed temperature, they tend to soften over a range of temperature. On heating, an amorphous solid gradually softens, becomes mobile and eventually acquires the properties of a liquid ; amorphus solids can, therefore, be regarded as super-cooled liquids of very high viscosity.

Sometimes a substance can exit in more than one crystalline form. In the case of elements, these different forms are called *allotropes* of the element. For example, diamond and graphite are allotropic forms of carbon. When a compound exists in two or more crystalline forms, as in yellow mercuric iodide and red mercuric iodide, the forms are called *polymorphs* and the phenomenon is *polymorphism.* When two different substances exist in the same crystalline form, these are known as *isomorphous* substances, e.g., potash alum and chrome alum.

11.11. Preparation of crystals :—

Crystals may be prepared ; *by concentrating a dilute solution, usually by heat and then cooling* ; The common method of obtaning a substance in crystalline form is to prepare a very concentrated solution of the substance at a higher temperature. On cooling, the solution becomes first saturated and on further cooling the solute comes out as crystals. If the process of cooling be made very slow, crystals separate in larger sizes.

A dilute solution may also be concentrated by evaporating the solution slowly till the crystals begin to appear at the edges. On cooling this concentrated (saturated) solution, the solute comes down in the form of fine crystals.

Experiment : *Preparation of alum crystals* :

About 50 c.c. of distilled water is taken in a beaker and heated over a wire gauze. Finely powdered potash alum is then slowly added to hot water with constant stirring till some alum remains undissolved at the bottom. Thus a saturated solution of alum in distilled water is prepared at high temperature. Then the burner is removed and the clear solution from the top is quickly filtered into another beaker. The hot filtrate is then kept undisturbed for slow cooling. As the filtrate cools, beautififul small octahedral crystals of alum would separate out from the solution. The crystals are separated from the liquid either by filtration or by draining off the saturated solution left after crystallisation. The crystals of alum are then dried by pressing with a dry filter paper. The saturated solution left after separation of the crystals is called **"mother liquor"**. In order to obtian a large crystal, a perfect crystal of alum is suspended into the clear saturated solution of alum by means of a thread as shown in Fig 11.6. The solute deposits itself on this tiny crystal and it grows in size. This is called "*seeding*" the saturated solution.

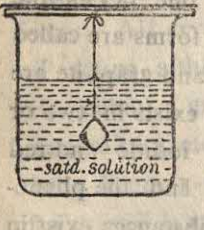


Fig. 11.6. Large size crystal

Evaporation of a solution at the ordinary temperature also yield crystals ; thus from a solution of sulphur in carbon disulphide, pale yellow rhrombic crystals of sulphur are deposited by the spontaneous evaporation of the volalite solvent.

(ii) by solidifying certain fused substances :—crystals are also formed when a substance is melted and the molten mass is allowed to cool slowly. Crystals appear on solidification. Molten sulphur on cooling gives needle-shapped crystals of monoclinic sulphur.

(iii) by sublimation i.e., by condensing the vapours of volatile solids :—volatile solids can sometimes be easily sublimed to obtain it in crystalline form. Thus a certain quantity of iodine when heated sublimes giving violet vapours, which condense to the solid directly in contact with a cold surface, yielding dark-grey shining crystals of iodine. By applying the same process, caystals of ammonium chloride, camphor, naphthalene etc. may be obtained.

11-12. Separation and purification of solids by crystalllsation :—

1. **Recrystallisation** :—When a crystalline solid is contaminated with small quantity of impurity (either as insoluble substance or as a soluble substance with different solubility), it can be purified by repeated crystallisation i.e., re-crystallisation, from suitable solvent. The purity of a solid may be ascertained by its melting point which must be sharp and fixed for a pure solid.

2. **Fractional crystallisation** :—This is a convenient method of separating the components of a mixture of two or more soluble solids in the pure state, provided their solubilties differ appreciably. When a concentrated solution of the mixture two soluble solids are made at a higher temperature, and allowed to cool slowly, it first gets saturated with the least soluble of the substances in solution, the excess of which, therefore, first deposits as crystals and separated by filtration. These crystals may be redissolved in a further quantity of boiling water and the process of crystallisation repeated. Re-crystallisation will ultimately produce the pure component. The filtrate, on concentration and cooling gives crystals of the more soluble component which are similarly filtered, re-crystallised, washed and dried. Thus two

solids like sodium chloride and potassium nitrate can be separated in the pure state by fractional crystallisation of their mixed solution. Madame Curie obtanied a fraction of a gram of radium salt from a ton of pitchblende by the process of fractional crystallisation.

11-13. Hydrated and anhydrous substance :—

Many solids, while crystallising out of their aqueous solutions yield crystals which contain definite number of water molecules taken up from the solution during their formation. These are called *hydrated crystals* and the water linked up with a molecule of the substance in the crystal is called *water of crystallisation.* This combined water is essentially responsible for the particular crystalline shape of the solid and also for their colour.

Thus, water associated with crystals as an essential part of their constitution and responsible for their crystalline shape, is known as ater of crystallisation or water of hydration.

Examples :—Blue vitriol, $CuSO_4$. $5H_2O$; green vitriol, $FeSO_4$, $7H_2O$; oxalic acid, $(COOH)_2$, $2H_2O$; sodium carbonate, Na_2CO_3 $10H_2O$; potash alum, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$; calcium chloride, $CaCl_2$, $6H_2O$ etc.

Substances which do not incorporate any water during crystallisation are said to be *anhydrous.* Sodium chloride, NaCl ; silver nitrate, $AgNO_3$; ammonium chloride, NH_4Cl ; potassium chlorate, $KClO_3$; etc. are all anhydrous, these salts crystallise without taking any water of crystallisation. So water is not an essential part of all crystals.

Generally, the water of crystallisation escapes when the hydrated salt is heated and anhydrous salt is produced. In doing so both the shape and the colour (if any) of the hydrated crystals are lost which can be restored by adding water again. This can be best illustrated with crystals of blue vitriol, $CuSO_4$. $5H_2O$. When these blue crystals are heated, the water escapes as vapour and the crystals are left as a white powder of anhydrous copper sulphate. On moistening this white powder, it immediately turns blue and slowly the blue crystals are reformed. This shows, water of crystallisation is responsible for the crystal form and blue colour of blue vitriol. Anhydrous white copper sulphate is often used to detect the presence of moisture.

11.14. **Determination of water of crystallisation :—**

The percentage of water of crystallisation in a given sample of a hydrate and also its formula can be found out by removing the combined water completely by careful heating, and weighing the given substance before and after the heating operations. The difference of the two weights gives the weight of the "water of crystallisation", from which the percentage of water of crystallisation can be found out.

Experiment : *To determine the water of crystallisation of barium chloride crystals.*

A clean and dry porcelain crucible with lid is carefully weighed. A small quantity of pure barium chloride crystals (1 to 2 gm) is taken in the cruicible and is weighed again. The crucible is then heated over Bunsen flame on a fireclay triangle (Fig 11-7), first gently and then strongly for about half-an-hour with the lid kept partially open for escape of water of crystallisation as steam. After heating, the crucible is allowed to cool in a desiccator and the crucible with its lid and the contents is weighed again. The crucible is again heated for about 10 minutes, cooled as before and weighed again. The weight should remain the same, if not, the process of heating, cooling and weighing is repeated till the final weight is constant.

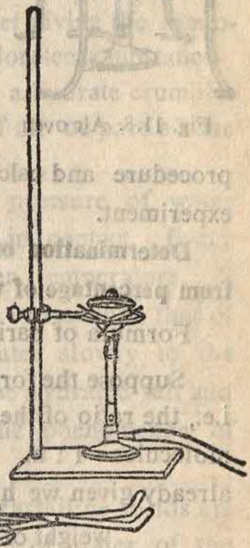


Fig 11.7. Determination of water of crystallisation of barium chloride

Calculation : Let, the wt. of the empty crucible + lid = x gm.

wt. of the crucible + lid + barium chloride crystals = y gm

wt. of the crucible + lid + anhydrous barium chloride = z gm.

∴ wt. of barium chloride crystals $=(y-x)$ gm.

and wt. of anhydrous barium chloride $=(z-x)$ gm.

Hence the wt. of water of crystallisation $=(y-z)$ gm.

∴ the percentage of water of crystallisation $=\frac{(y-z)}{(y-x)}\times 100$.

N.B. The removal of water of crystallisation from the hydrated salts has been made by strongly heating with a Bunsen flame directly in case of hydrated barium chloride, calcium chloride etc. which in anhydrous condition can withstand very high temparature without decomposition. But in case of hydrated crystals, like, blue vitriol, $CuSO_4, 5H_2O$ or potash alum, direct heating with Bunsen flame cannot be applied to remove water of crystallisation because these salts decompose at such high temperatures. Their water of crystallisation are usually determined by carefully heating the crystals on a watch glass in an air oven (Fig 11-8). where heating can be regulated upto the desired temperature. The procedure and calculation are the same as shown in the previous experiment.

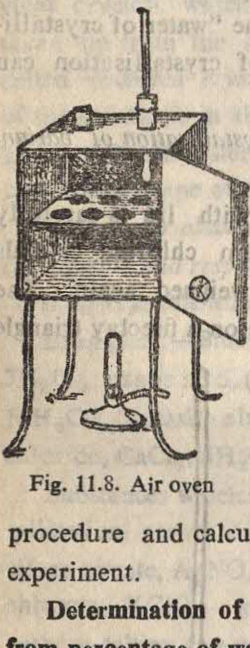


Fig. 11.8. Air oven

Determination of the molecular formula of the hydrated salt from percentage of water of crystallisation :

Formula of barium chloride crystals—

Suppose the formula of the hydrated molecule be $BaCl_2, nH_2O$, i.e., the ratio of the no. of molecules of anhydrous $BaCl_2$ to H_2O, molecules = 1 : n. Therefore, according to the experimental data already given we have,

$$\frac{\text{weight of anhydrous } BaCl_2/\text{mol. wt. of } BaCl_2}{\text{weight of water of crystallisation/mol. wt. of } H_2O}=\frac{1}{n}$$

Or, $\frac{(z-x)/208\cdot3}{(y-z)/18}=\frac{1}{n}$ (mol. wt. of $BaCl_2=208\cdot3$)

The experimental result shows that the percentage of water of crystallisation in barium chloride crystals is 14·73.

$$\therefore \quad \frac{(100\text{-}14{\cdot}73)/208{\cdot}3}{14{\cdot}73/18}=\frac{1}{n}\text{ ; which give } n\approx 2.$$

Hence, the required formula is $BaCl_2, 2H_2O$.

In the same way the formula of the other hydrated salts like, blue vitriol, alum etc. can be determined.

11-15. Efflorescence and Deliquescence :

There are certain hydrated crystals, like $Na_2CO_3, 10H_2O$, which gives up slowly its water of crystallisation to the atmosphere at the ordinary temperature, when left exposed to the air, either partly or completely forming a lower hydrate or the anhydrous compound. In this process the crystals often crumble down into a powder. This phenomenon is called *efflorescence* and the hydrates are known as efflorescent substances. Thus the crystals of sodium carbonate, $Na_2CO_3, 10H_2O$. loses 9 molecules of its water of crystallisatian (per molecule) when kept exposed to air at the room temperature and falls to powder giving the monohydrate, Na_2CO_3, H_2O. It is, therefore an efflorescent substance.

So. Efflorescence is a phenomenon in which a hydrate crumbles to powder on exposure to air, due to loss of all or part of the water of crystallisation.

The stability of a hydrate depends on the pressure of water vapour in the atmosphere with which it is in contact. Every hydrate has a definite vapour pressure at a given temperature. If the pressure of water vapour in the atmosphere is less than that of the hydrated crystal, the latter will give up water slowly to the atmosphere to attain equilibrium between the hydrated salt and its surroundings, and falls to a powder. The phenomenon of efflorescence is thus observed.

In some cases, the vapour pressure of the crystalline solids are very small, much less than the vapour pressure of water of the atmosphere. When such substances are kept exposed to air, they absorb water from the atmosphere and turn into solution by dissolving in the water absorbed. This phenomenon is known as *deli-*

quescence and the substances showing this property are called deliquescent substances. Thus when some solid calcium chloride is kept on a watch glass, it quickly absorbs moisture from air, becomes sticky and finally dissolves and passes into a solution. Calcium chloride is a deliquescent substance. Magnesium chloride ferric chloride, caustic soda, etc. are all deliquescent. So, deliquescence is a phenomenon in which a solid, when exposed to the atmosphere. absorbs moisture from air and finally dissolves in the absorbed water.

Pure sodium chloride is not a deliquescent substance. The commercial sodium chloride often behaves as a deliquescent substance, because it contains some calcium and magnesium chlorides as impurities.

Some substances such as quick lime, anhydrous copper·sulphate etc., absorb moisture on exposure to damp air but do not dissolve in it ; these are called *hygroscopic* substances.

COLLOIDS

11-16. The Colloidal State :

Thomas Graham in his classical researches on diffusion of various substances in liquid media, observed that almost all inorganic compounds like acids, bases and salts and also many organic compounds e.g., urea, sugar etc. would diffuse quite rapidly in solution and could readily pass through animal and vegetable membranes. On the other hand, substances like glue, starch, milk albumen, proteins, silicic acid etc. diffused but very slowly and could not pass through the membranes. Graham named the former class as *crystalloid* since most of them could be readily obtained in the crystalline state. The other class of compounds occured usually in a non-crystalline form was named *colloid,* from the Greek word *kolla,* meaning glue, which was a typical member of this class. In this way Graham differentiated between two classes of matter, the crystalloid and the colloid.

But in the light of later researches, this distinction between crystalloids and colloids as different kinds of matter has been dropped. There are many substances which may exist in solution as crystalloids or as colloids, depending upon conditions. For instant, soap is colloidal in water and crystalloidal in alcohol. Common salt, which is a typical crystalloid in aqueous solution, may be brought into a colloidal state in benzene. Besides, many colloidal substances have crystalline structure. For this reason, it is best to speak of a *colloidal state* instead of *colloids*. In fact it is the size of the particle which decides if a substance will remain in the colloidal state.

In a true solution, the solute distributes in the solvent as ions or individual molecules. So. whenever a substance disperses itself in a medium as particles having 10^{-8} cm diameter, it would form a solution in that medium. Due to their extreme smallness, the particles cannot be seen even under a microscope and cannot be separated by filtration through ordinary filter paper. A suspension, on the other hand, is a heterogenous system which contains finely divided, insoluble, solid particles having sizes approximately $10^{-4} \sim 10^{-5}$cm in diameter, which are visible to the naked eye, or, at least, in a microscope and settle out gradually under gravity. Between these two extremes exists the colloidal system in which the sizes of the particls are $10^{-5} - 10^{-7}$ cm in diameter, i.e., particles are larger then molecules but are not large enough to be seen under the microscope. The colloidal particles do not settle under gravity and cannot be separated by filtration, they pass through ordinary filter paper. It is heterogeneous and is not a true solution. The approximate size (diameter) of the particles present in the three states are give below :

Coarse Suspension	**Colliodal particles.**	**Molecular diameter.**
10^{-3} to 10^{-5} *cm*	10^{-5} to 10^{-7} *cm*	10^{-7} to 10^{-8} *cm*
i.e., > 100 $m\mu$	i.e., 100 $m\mu$ to 1 $m\mu$	i.e., 1 $m\mu$ to 0·1 $m\mu$

[1 $m\mu$ = millimicron = 10^{-7} *cm* ; μ = micron = 10^{-4} *cm*.]

In the light of the above discussions, a colloidal solution may be defined as follows :

A Colloial solution is a stable two-phase, heterogeneous (although apparently homogeneous) system in which one phase (usually solid) is distributed or dispersed throughout the other (often a liquid) as finely divided particles ranging from 10^{-5} to 10^{-7} cm approximately in diameter. The substance which disperses itself in such fine particles is in the colloidal state and is known as the disperse phase and the medium in which dispersion occurs is called the dispersion medium.

As already stated the colloidal solutions are not true solutions. They are, therefore, generally referred to as the colloidal systems or colloidal dispersions.

11-17. Types of Colloidal dispersions :

The desperse phase and the dispersion medium may be solid, liquid or gas, except that two gases cannot form a colloidal system as gases are completely soluble in each other producing homogeneous mixtures. According to the state of aggregation of the disperse phase and dispersion medium, there may be different types of colloidal dispersions which are tabulated below :

Disperse Phase	Dispersion medium	Name of the colloid	Examples
Gas	Liquid	foams	whipped cream, soap froth
Liquid	Gas	aerosols	mist, cloud, fog
Liquid	Liquid	emulsions	milk, butter
Solid	Gas	aerosols	smoke, dust
Solid	Liquid	sol, gel	sols of starch, gum, proteins, colloidal sulphur, gold, silicic acid, mud, blood, etc.

Of all these types of colloids, *sols* and *emulsions* are most important. Sols are the colloidal systems where disperse phase is solid and dispersion medium is liquid. A sol whose despersion medium is water is known as *hydrosol* or simply *sol*, for example ferric hydroxide sol, silver iodide sol, gold sol etc. If alcohol is the despersion medium, it is called *alcosol*, and so on. sometimes sols are obtained in a highly concentrated state and they have the property of setting to a semi-solid jelly-like state. These are called *gels* A liquid colloidally dispersed as droplets in another liquid gives rise to *emulsions*. Milk is an emluusion of fine droplets of fat in water. Many pharmaceutical preparations are emulsions, e.g., Cod-liver oil emulsion.

Sols are frequently subdivided into two classes : on the basis of solvent affinity : (i) lyophobic sols and (ii) lyophilic sols

(i) *lyophobic* (*solvent hating*) *sols* :—In such sols, there is no perceptible affinity between the disperse phase and dispersion medium, and consequently the disperse phase tends to come out of the colloidal state as visible precipitates. The sols of metals such as Au, Ag etc., sulphur, many hydroxides, sulphides, etc. in aqueous dispersion medium are lyophobic colloids. These sols are sometimes called *irreversible sols*, for once precipitated out, it is not generally easy to get it back in the colloidal state.

(ii) *lyophilic* (*solvent loving*) *sols* :—In such a colloidal system the disperse phase exhibits great affinity for the dispersion medium and consequently many substance forming lyophilic sols, undergo spontaneous dispersion into the colloidal state in coming in contact with the dispersion medium. Lyophilic sols are very stable. Typical lyophilic colloids are obtained with glue, starch agar-agar, dextrin, gelatin, etc. in water. On evaporation or cooling of lyophilic sols, solids are separated which can be reconverted into sols by adding the solvent. Lyophilic sols are, thus, reversible in character.

Sols are called hydrophobic and hydrophilic when the dispersion medium is water.

11-18. Preparation of Colloidal solutions :

Lyophilic colloids are often prepared simply by mixing the substances with the liquid medium, if necessary, with heating. Lyophilic colloid particles are heavily solvated.

For the preparation of lyophobic colloids, there are two general methods : (i) *Condensation* methods, in which particles of colloidal size grow up by the agglomeration of substances dispersed in the molecular state; and (ii) *Dispersion* or disintegration methods, in which larger particles of the substances are mechanically broken down into particles of colloidal size.

(i) *Condensation methods* : Particles of colloidal size are obtained by this mehod as a result of different types of chemical reaction, such as reduction, oxidation, hydrolysis etc. Some examples are given below :

(a) *Gold sol* : (Zigmondy's method). A gold sol is easily prepared by *reduction* of gold chloride solution (auric chloride) with formaldehyde.

(b) *Arsenious sulphide sol* : The beautiful yellow coloured arsenious sulphide sol is formed by *metathesis*, by passing H_2S into a soution of arsenious oxide in water. $As_2O_3 + H_2S \rightarrow H_2O + AS_2S_3$ (colloid)

(c) *Ferric hydroxide sol* : The addition of a few ml. of concentrated $FeCl_3$ solution drop by drop to large volume of boiling water poduces colloidal ferric hydroxide by *hydrolysis* :

$$FeCl_3 + H_2O \rightarrow HCl + Fe(OH)_3 \text{ (colloid)}$$

(d) *Sulphur sol* : A milky sulphur sol is often prepared by *oxidation* of aqueous solution of H_2S by SO_2 : $H_2S + SO_2 \rightarrow H_2O + S$ (colloid)

Sulphur sol can also be obtained by *solvent exchange* method. When an alcoholic solution of sulphur is added to a large volume of water, white sulphur sol is formed.

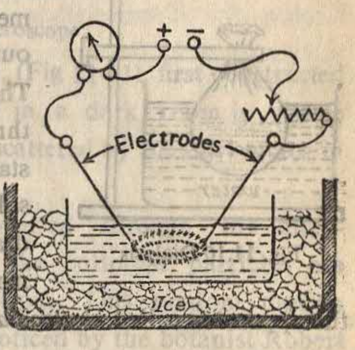
(e) *Silicic acid sol* : This may be prepared by adding slowly a dilute solution of sodium silicate to a large excess of dilute HCl ; $Na_2SiO_3 + HCl \rightarrow 2NaCl + H_2SiO_3$ (colloid)

(ii) *Dispersion methods* : In this method larger or massive particle of the substances are brought down to the colloidal dimension as follows—

(a) *Mechanical dispersion* : Occasionally, ordinary grinding of the coarse particles with solvent in a *colloid mill* will produce a colloidal solution.

(b) *Electrical disintegration* : *Bredig's method.* Metal colloids are prepared by this method e.g., sols of Au, Ag, Cu, etc. A direct current electric arc is struck between two metal electrodes (Fig 11-9), held under water and the metal sol is formed. The metal is first vaporised by the arc and it condenses to fine colloidal particles in water. So this method involves both dispersion and condensation.

Peptisation : it is another dispersion method for preparing colloidal solutions. It is a method of re-dispersion of a precipitated substance. Thus when freshly precipitated hydrated ferric oxide is stirred with small amount of ferric chloride, a stable $Fe(OH)_3$ sol is formed.



11.9. Fig. Bredigs method

11-19. Purification of the colloid : Dialysis :

Colloidal dispersions generally contain some electrolytes (crystalloids) during their preparation. Though certain amount of electrolyte is required for their stability, but the sols will be unstable if large amount of electrolytes are present. So to prepare stable colloidal sols, the crystalloids should be removed from the colloids just after their preparation. Colloidal particles pass through the pores of ordinary filter paper hence they cannot be separated from the electrolytes by ordinary filtration. Bu·tthere are some membranes, such as parchment paper, collodion film etc. through which solvent molecules or solutes can easily pass but colloidal particles cannot. With such filters, it is possible to separate a colloid from its mixture with other solutes or ions. This method of separation is known as **dialysis.** Thus, process of separating and purifying a colloid from the crystalloids by means of diffusion through a membrane is called dialysis.

Experiment : The apparatus used for this purpose is known as a dialyser, which in its simplest form consists of a parchment or collodion bag half immersed in water (Fig 11-10). A mixture of a colloid and a crystalliod, say one of starch and potassium iodide solution, is taken in the parchment paper bag (dialyser) and the outside water is repeatedly changed. The ions of potassium iodide pass out through the parchment filter but the starch is retained and the colloidal solution of starch is left inside the dialyser in a pure state. The process may be hastened in an electric field in the apparatus called *electrodialyser.*

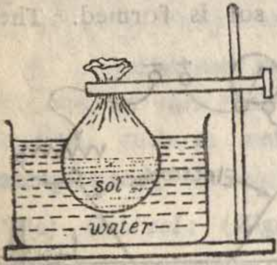


Fig. 11.10 Dialysis

11.20. **Properties of colloids :**

The colloidal systems extibit some charactersistic properties of their own, which are given below :

(1) *Colour* **:** The colour of a colloidal solution is generally different from the orginal colour of disperse phase and the colour depends upon the size of the colloidal particles. A gold sol usually possesses colour varying from red to bluish red ; silver sol is grey or greenish grey etc.

(2) *Tyndall effect* : Colloidal particles are too small to be observed under an ordinary microscope. The particles, however, reveal their existence if a strong narrow beam of light is allowed to pass through such a solution in a darkened room at right angles to the line of vision of a high-power microscope. The light is scattered by the colloid particles and bright specks of light are visible when viewed through the microscope against a dark back-

ground. The phenomenon of scattering of light by the colloidal particles is called **Tyndall effect** and the apparatus for viewing the particles is called **ultramicroscope**, (Fig 11-11), first constructed and used by Zsigmondy. A sunbeam in a dark room is visible by the same effect, the light being scattered by the dust motes in the air.

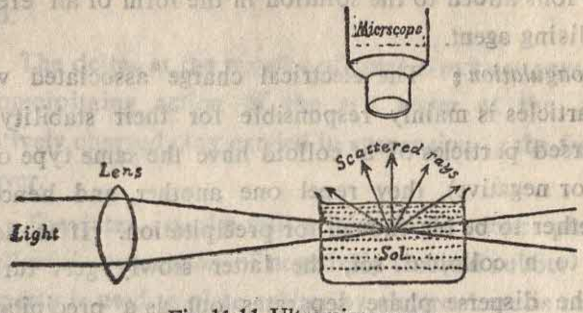


Fig 11·11 Ultramicroscope

(3) *Brownian motion*: When viewed through the ultramicroscope and examined carefully, the colloidal particles are found to be in a ceaseless random motion. This random motion of the colloid particles was first noticed by the botanist Robert Brown in pollen grains dispersed in water, and is called 'Brownian motion'. The motion is caused by the unbalanced impacts of the solvent molecules striking against the suspended particles. The Brownian motion constitutes the most convincing evidence for the real existence of molecules and for their random motion (Fig 11-12).

(4) *Electrophoresis* : When a colloidal solution is placed in an electric field, colloidal particles are found to move to either the cathode or the anode, showing that the colloidal particles are electrically charged with respect to the dispersion medium. The motion of the charged colloid particles towards the electrodes under a potential gradient is called electrophoresis or cataphoresis. Colloidal particles of clay, arsenious sulphide, metals such as Au, Ag, Pt etc. carry negative charges, whereas

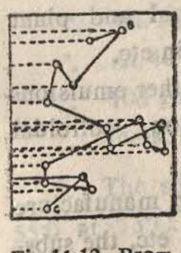


Fig 11·12. Brownian motion

$Fe(OH)_3$ basic dyes, haemoglobin etc. carry positive charges. The particles acquire their charges generally by adsorption on their surface of ions added to the solution in the form of an electrolyte as a stabilising agent.

(5) *Coagulation* : The electrical charge associated with the colloid particles is mainly responsible for their stability. Since the dispersed particles of a colloid have the same type of chrage (positive or negative), they repel one another and hence cannot come together to be big enough for precipitation. If an electrolyte is added to a colloidal sol, the latter slowly gets turbid and finally the disperse phase separates out as a precipitate ; this phenomenon is known as precipitation or coagulation and the precipitate is a coagulum. Coagulation is due to the neutralisation of the charge on the colloid particles by the oppositely charged ions of the added electrolyte. The coagulating power of an electrolyte depends upon the valency of the coagulating ion. The higher the valency of the coagulating ion, smaller is the quantity of ion required for preciptitation of a given amount of colloid. For example, bivalent sulphate ions are about 50 times more effective than univalent chloride or nitrate ions in coagulatng positively charged ferric hydroxide sol.

11·21. Importance of the study of colloids :

Colloids play an important role in our daily life, in industry and, as a whole, in science and technology, only a few of its applications are mentioned here.

(i) Many of our foods, like milk, tea, coffee, butter, ice-cream, etc. are colloidal.

(ii) Many of life-sustaining fluids in the animal and plant bodies are colloidal ; e.g., protoplasm, blood, albumin etc.

(iii) Many pharmaceutical preparations are either emulsions or colloidal suspensions ; e.g., cod-liver oil emulsion, colloidal gold sol, milk of magnesia etc.

(iv) In many industries such as, tanning, dyeing, manufacture of paints, photographic plates, lubricating grease. etc. the substances treated are more or less of colloidal nature.

(v) In cleaning, the soap is used in a colloidal form to take away grease by adsorption, so that dirt is set free and removed.

(vi) The deltas at the mouths of great rivers are caused largely by the precipitaing action of the salt water of the ocean on the negatively charged clay carried in suspension in the fresh water of the river.

(vii) The latex, i.e., the milky juice that a rubber plant yields, is a colloidal suspension of negatively charged rubber particles, this property is used to plate rubber by electrophoresis on various objects. Gloves, hot water container etc. are made in this way.

NUMERICAL PROBLEMS

1. At 25°C, on evaporation to 62 gm. of a saturated solution of sodium carbonate, 12 gm of solid residue was left. What is the solubility of sodium carbonate at 25°C ?

$$62 \text{ gm} - 12 \text{ gm} = 50 \text{ gm}$$

That is 50 gm of water can dissolve 12 gm of sodium carbonate for saturation or, 100 gm of water can dissolve $12 \times 2 = 24$ gm. Sodium carbonate for saturation.

∴ at 25°C, the solubility of sodium carbonate = 24.

2. At 45°C, 75 c.c. of a saturated solution of nitre contain 40 gms of the salt. If the specific gravtiy of the solution be 1·2, determine the solubity of nitre at 45°C.

wt. of 75 cc. of the satuted solution $= 75 \times 1{\cdot}2 = 90$ gms.

∴ wt. of water $= 90 - 40 = 50$ gm.

∴ At 40°C, 50 gm water dissolve 40 gm. of nitre.

∴ 100 gm of water dissolve 80 gm of nitre.

∴ the solubility of nitre at 45°C = 80.

3. The solubility of copper sulphate is 19·0 at 15°C and 55·0 at 75°C. What weight of crystals would be deposited if 77·5 gm of copper sulphate solution saturated at 75°C is allowed to cool to 15°C ?

At 75°C, 100 gm water can dissolve 55 gm of $CuSO_4$

∴ the weight of the solution = 155 gm.

and at 15°C, 100 gm of water can dissolve 19 gm of $CuSO_4$

∴ the weight of solution = 119 gm.

Hence, it is obvious that on cooling 155 gm of the solution from 75°C to 15°C, (155 − 119) = 36 gm $CuSO_4$ will be deposited.

∴ 77·5 gm saturated solution will deposit $\frac{36 \times 77 \cdot 5}{155}$

$= 18$ gm $CuSO_4$

4. The residue from 1 gm of crystallised barium chloride after it has been heated till no further loss of weight occured, weighed 0·853 gm. What is the formula of the crystallised salt ? (At. wt. of Ba = 137)

Let 1 molecule of hydrated barium chloride contain n molecules of water of crystallisaton, So its molecular 'formulla is $BaCl_2, nH_2O$.

∴ the mol. wt. of the crystallised salt $= 137 + 2 \times 35 \cdot 5 + n \times 18$

$= 208 + 18n.$

Now, $(208 + 18n)$ gm crystallised salt contain $18n$ gm water.

∴ 1 gm of crystallised salt contains $\frac{18n}{208 + 18n}$ gm water.

From the data given, 1 gm of crystallised salt contain $1 - \cdot 853$

$= \cdot 147$ gm water.

i.e., $\frac{18n}{208 + 18n} = \cdot 147$ or, $18n = 208 \times \cdot 147 + 18 \times \cdot 147n$

or, $18(1 - \cdot 147)\,n = 208 \times \cdot 147$

$\therefore n = \frac{208 \times \cdot 147}{18 \times \cdot 853} = 1 \cdot 99 \approx 2.$

Hence the formula of the crystallised salt is $BaCl_2, 2H_2O$.

Exercise—11

1. (a) Define and illsutrate the following : (i) solution, (ii) suspension, (iii) colloidal dispersion, (iv) emulsion.

   (b) Distinguish between saturated, unsaturated and supersaturated salutations.

   (c) Can a saturated solution be a dilute solution at the same time ? Can a coneentrated solution be unsaturated ? Give examples.

2. (a) What is "solubility" ? Explain it with an example. On what factors does the solubility of a solid in a liquid depend ?

   (b) How would you determine the solubility of KNO_3 in water at room temperature ? Name a liquid and a gas which are highly soluble in water.

   (c) "The solubility of potassium nitrate is 40". This statement is meaningless. Explain.

3. (a) What are solubility curves ? How are they obtained ? What informations are supplied by the curves ? what is the significance of a break in the solubility curve ?

   (b) The following table gives the solubilities of KCl and $NaNO_3$ at different temperatures :

	15°	25°	50°	75°	100° C
KCl	32·4	35·5	42·6	49·7	56·7
$NaNO_3$	84	91	112	140	180

   (i) Draw the two solubility curves and find out the solubility of the salts at 40° C and at 60° C.

   (ii) If a mixture of the concentrated solution of these two salts be cooled down to 60° C, which salt would seperte first and why ?

4. (a) What are crystal ? In what different ways can crytals be obtained ? Explain how you would grow a large crystal of alum. How does ordinary crystallisation differ from fractional crystallisation ?

   (b) It is possible for a substance to exist in different crystalline forms or for different substances to have the same crystalline form r Illustrate each with examples.

   (c) What is "Water of crystallisations ? Give examples. Describe how would you determine the percentage of water of crystallisation in copper sulphate crystals.

5. Explain, with reason, the phenomena of efflorescence and deliquescence. Give examples. What is a hygroscopic substance ?

6. (a) What is a colloidal solution ? How does it differ from a true solution ? Mention some of the special propeties of colloids.

6. (b) What are lyophobic and lyophilic colloids ? Explain with examples. How would you prepare fairly pure samples of (i) ferric hydroxide sol, (ii) platinum sol.

(c) Write explanatory notes on (i) Dialysis, (ii) Tyndall effect, (iii) Brownian movement, (iv) cataphoresis, (v) coagulation.

7. At 16° C, 30 gm. water was saturated when 10·65 gm common salt was added. What is the solubility of the salt at 16° C ? [35·5]

8. At 50°C, 75 gm of an unsaturated solution of common salt was taken. On evaporation, it gave a solid residue of 15 gm. salt. How much salt has to be added to 100 gm of this solution to saturate it ? The solubility of common salt at 50° C is 40. [12 gm].

9. 50 gms of lead nitrate are dissolved in 75 cc. of boiling water. Find the weight of the solute that will crystallise out when the solution is cooled down to 20° C. Solubility of lead nitrate at 20° C is 54·4 [9·2 gm].

10. The hydrated megnesium sulphate is represented by the formula $MgSO_4$ xH_2O. If it contains 51·22% water of crystallisation, find the value of x. [7]

11. 2·5gm of blue vitriol when strongly heated gave 1·6 gms of anhydrous salt. Calculate the percentage of water in the blue vitriol and find out the formula of the crystal. (Cu = 63·5 S = 32) [(i) 36%, (ii) $CuSO_4$, $5H_2O$]

12. The solubility of potassium nitrate in water at 75°C is 155 and at 20°C it is 31. What weight of potassium nitrate must be taken to give 100 gms of crystal, when a saturated solution at 75° C is cooled to 20° C [125 gm].

CHAPTER—XII

ELECTROLYSIS

12·1. Conductors and Non-conductors : Electrolytes.

Substances can be classified as *conductors* and *non-conductors* according to their behaviour towards the passage of electric current through them. The substances which strongly resist the flow of electricity and practically do not allow any current to pass through them, are called *non-conductors.* Glass, wood, wax, mica, rubber, sulphur, kerosene etc., are some of the examples of non-conductors. On the other hand, there are substances through which electric current can easily pass, these are called *conductors.* Many metals (like Cu, Ag, Au, Pt, Fe etc), some non-metals (like graphite, gas-carbon, selenium etc), and substances like, acids bases and salts, either in solution or in fused state are examples of conductors.

The conductors are again divided into two classes,—

(ii) *Electronic or metallic conductors*—such as Au, Ag, Cu, graphite, mercury selenium etc. They conduct electricity by the actual transport of electrons and there is no permanent change of the conductor due to passage of electricity except the heating effect.

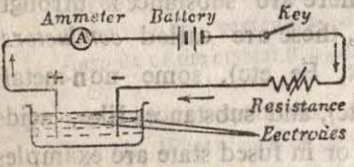
(ii) *Electrolytic conductors or electrolytes*—such as acids, bases and salts in the fused state or in aqueous solution. They conduct electricity by the migration of ions. This involves a transport of matter from one part of the conductor to another leading to the decomposition of these substances. Electrolytes cannot conduct electricity in the solid state.

Compounds which do not conduct electric current in aqueous solution or in the molten state are called *non-electrolytes.* Solutions of sugar, urea, etc, or liquids like alcohol, kerosene which are non-conductors, are examples of non electrolyte.

Though the electrolytes are fairly good conductors, they are far less conducting than pure metals. It is also found that solution of weak organic acids and bases are very feeble conductors in comparison with those of strong acids, strong bases and salts, and so the former are called *weak electrolyte*, the latter *strong electrolytes.*

Electrolysis is the process of the condutction of electric current by an electrolyte. either fused or in solution, with the accompanying chemical decomposition of the substance.

Elecetrolyis is generally carried out in a vessel called voltameter or electrolytic cell (Fig 12-1). The vessel contains the electrolyte (molten or in solution) in which two rods or plates of metals or graphite are kept partially immersed, through these rods or plates, the current enters and leaves the electrolyte. These are called electrodes. The electrode which is connected with the positive terminal of a battery and through which the current enters the electrolyte is known as the **anode** or the positive electrode. The electrode which is connected to the negative terminal of the battery and through which the current leaves the electrolyte is the negative electrode and is called the **cathode.** Generally copper and platinum electrodes used during electrolysis. However, in some cases, electrodes made of nickel, graphite, iron etc. are also applied. It is easy to conceive that the anode or the positive electrode has a deficiency of electrons and would readily accept electrons, whereas the cathode or the negative electrode, has an abundace of electrons and would easily give away electrons. Though the current flows through the bulk of the electrolyte but electrolysis occurs only on the eletrodes.



12.1. Voltameter

12·2. **Simple cases of Electrolysis** :

(i) *Electrolysis of water*—Pure water is a bad conductor of electricity as if a very feeble electrolyte. But if water is acidulated with small amount of HCl or $H_2SO_4^{=}$, it behaves as a good conductor. On electrolysis, using pt-electrodes, **hydrogen** is liberated at the **cathode** and **oxygen** at the **anode.**

(ii) *Electrolysis of sodium chloride solution*—When sodium chloride solution is electrolysed using graphite electrodes, **hydrogen** gas is obtained at the **cathode** and **chlorine** is obtained at the **anode.**

(iii) *Electrolysis of copper sulphate solution*—When copper sulphate solution is electrolysed between platinum electrodes, metallic **copper** will be deposited at the **cathode** and **oxygen** will be evolved at the **anode.**

12·3. Mechanism of Electrolytic conduction : Arrhenius theory of electrolytic dissociation.

In order to explain the behaviour of electrolytes in conducting electricity and the consequent chemical changes, attempts had been made from time to time by a number of scientists like Grothus, Clausius and others. But a clear and comprehensive picture of the mechanism of the flow of electricity through electrolytes and the consequent electrolysis was presented first by the sweedish scientist Arrhenius (1887) in his well known *theory of electrolytic dissociation.* The basic postulates of the theory which Arrhenius proposed with a few modifications subsequently made may be stated as follows :

(i) The molecules of an electrolyte either in the molten state or when dissolved in an ionising solvent (e.g., water), dissociate spontaneously into positively and negatively charged particles. These electrically charged particles which are derived from atoms or radicals by loss or gain of one or more electrons, are called *ions.* The positively charged ions are called *cations* and the negatively charged ions, *the anions.* The metals and hydrogen produce cations and the non-metals and acid radicals from anions. This process of breaking up of electrolytes in solution into ions is called ionic or electrolytic dissociation, and is reversible in character. The electrolyte molecules break up partly into ions which in turn reunite to form the undissociated molecules. Thus an equilibrium is established between the ions and the undissociated molecules of the electrolyte. Molecules of sodium chloride, sulphuric acid, caustic soda, zinc sulphate, for example, dissociate in their aqueous solutions in the following way :

$$NaCl \rightleftharpoons Na^+ + Cl^- \qquad NaOH \rightleftharpoons Na^+ + OH^-$$

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--} \qquad ZnCl_2 \rightleftharpoons Zn^{++} + 2Cl^-$$

The properties of the charged particles are entirely different from those of the netural atoms.

(ii) The number of cations may not be equal to the number of anions produced. But since the solution as a whole is electrically neutral, the total positive charge carried by the cations must be equal to the total negative charge carried by the anions. The number of unit charges carried by an ion is found to be equal to the valence of the atom or radical from which the ion is produced.

Electrolyte molecule	Cation	Anion	Total positive charge	Total negative charge
$HCl \rightleftharpoons$	H^+	$+ Cl^-$	1	1
$Ca(OH)_2 \rightleftharpoons$	Ca^{++}	$+ 2OH^-$	2	$2 \times 1 = 2$
$FeCl_3 \rightleftharpoons$	Fe^{+++}	$+ 3Cl^-$	3	$3 \times 1 = 3$
$Al_2(SO_4)_3 \rightleftharpoons$	$2Al^{+++}$	$+ 3SO_4^{--}$	$2 \times 3 = 6$	$3 \times 2 = 6$

(iii) The ionisation of electrolytes in solution is not always complete. The degree of ionisation, i.e., the extent to which an electrolyte dissociates into ions, largely depends on several factors like, dilution, temperature, presence of other ions in solution, and above all, on the nature of the electrolyte and the solvent or ionising medium. The electrolytes which show a very high degree of ionisation even at ordinary dilution and whose aqueous solutions are good conductors of electricity are called *strong electrolytes.* Mineral acids like HCl, H_2SO_4, HNO_3, bases such as $NaOH$, KOH etc. and all salts belong to the class of strong electrolytes. On the other hand, substances which ionise to a very small extent at ordinary dilution and have low conducting power are known as *weak electrolytes.* The acids like CH_3COOH, H_3BO_3, carbonic acid, and bases like NH_4OH etc. are examples of weak electrolytes. Water is a very weak electrolyte ; one out of 1 million molecules dissociate as $H_2O \rightleftharpoons H^+ + OH^-$.

The degree of dissociation of an electrolyte steadily increases with dilution and becomes complete only in infinitely dilute solutions when the electolyte completely dissociates into ions. It is however now known that the strong electrolytes, remain practically completely dissociated at all concentrations.

With the increase in temperature the degree of dissociation generally increases.

The strong electrolytes ionise almost completely in a polar ionising solvent like water, but may behave as non-electrotyte, in a non-polar solvent.

(iv) It is the ions, not the undissociated molecules, which are responsible for carrying electricity through the electrolyte when an electric current is sent through the electrolyte by connecting the two electrodes to the terminals of a battery. The positively charged cations move towards the negative electrode or cathode, the negatively charged anions move towards the positive electrode or anode. (Fig 12-2). On reaching the cathode, cations accept the electron(s) from the cathode and are neutralised. Similarly, when the anions reach the anode, they give up electron(s) to the anode and are neutralised. As a result, the neutral atoms or radicals are librated at the elecrodes. This explains why the electrolysis occurs at the electrodes and not throughout the solution.

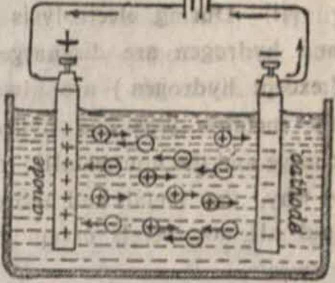


Fig 12·2 Conduction of electricity in a solution

The cations thus help in transferring the electrons from the cathode to the electrolyte and anions help in transferring from the electrolyte to the anode. Although the cations and anions migrate in opposite directions, both help in transferring electrons in the same direction from cathode to anode through the electrolyte. The electricity in thus conducted by the charged ions. The current is said to flow from anode to cathode, but in fact, the electrons flow from the cathode to anode via the solution of the electrolyte inside the vessel and from the anode to cathode through the connecting wire out side the elctrolytic cell.

(v) The conducting power or conductance of an electrolytic solution depends upon (i) the charge carried by the ions, (ii) the number of ions, and (iii) the velocity of the ions. A 0·1 (M) HCl solution has a much higher conductivity than 0·1 (M) NaCl solution, because the velocity of H^+ ions is much greater than that of Na^+ ions. Similarly a normal solution of HCl is more conducting than a normal solution of CH_3COOH, because the former has much larger number of H^+ ions than that in the latter in equal volumes.

12·4. Some relevant points from the dissociation theory :

(i) The electric current does not cause dissociations of the electrolytes into ions. It exerts only a directive effect on the ions already present in the solution due to spontaneous dissociation of the electrolyte.

(ii) During electrolysis it is always found that the metals and hydrogen are discharged at the cathode and all nonmetals (except hydrogen) are always discharged at the anode. Hence the metallic ions and hydrogen ion must be carrying positive charge and the non-metallic ions must carry negative charge. That is why, the metals and hydrogen are called *electropositive elements* and all non-metals except hydrogen are called *electronegative elements*.

(iii) Arrhenius theory to account for the increasing ionisation and conductivity of the electrolyte with dilution holds good in case of weak electrolytes. But this view is not fully applicable in case of strong electrolytes, which remain completely ionised at all dilution.

(iv) In any reaction between electrolytes in solution, it is really the ions that interact. When $AgNO_3$ solution is added to the solution of any choloride salt, always the same white precipitate of AgCl is produced. This is possible only if we assume this as an ionic reaction between Ag^+ and Cl^- ions.

$$X^+(Na^+)+Cl^-+Ag^++NO_3^-\rightarrow AgCl\downarrow+X^+(Na^+)+NO_3^-$$

As such, $AgNO_3$ is a reagent for choloride ion. Every precipitation reaction in inorganic chemistry has the same explanation.

(v) The nature and characteristics of an ion which is charged atom or radical, are absolutely different from those of the atom from which it is formed by loss or gain of electron(s). We now know that cations are formed when an atom gives away one or more electrons. Anions are formed by acceptance of one or more electrons : $Na-e=Na^+$, $Cl+e=Cl^-$.

(vi) All electrolytes are electrovalent or ionic compounds. In fact, the molecules of most of the electrolyes are made up of positively charged and negatively charged ions even in the solid crystalline state which are held firmly by strong attractive force. On dissolving in an ionising solvent, these ions separate leading to the dissociation of the electrolyte. The molecules of covalent compounds like sugars, urea etc, do not produce ions in solution and hence the aqueous salutions do not conduct electricity. Anhydrous hydrogen chloride, though a covalent compound acts as a strong electrolyte in aqueous solution as the molecules are highly polar and form free ions by reacting with water ; $HCl+H_2O\rightarrow H_3O^++Cl^-$.

12·5. Examples of Electrolysis :

The products of electrolysis which are finally obtained at the cathode and at the anode depend on the nature of the electrolyte and the electrode use. The concentration of the ion in the electrolyte also has an influence on the discharge of ions. Generally higher concentration of the ion tends to promote its discharge at the electrode. When several cations (or anions) are present in the electrolyte, selective discharge of a particular ion in preference to the others depends on its position in the electrochemical series (see Sec. 12.13.) The lower the position of the metal in the electro-chemicals series, the greater is the tendency to be librated at the cathode. Selective discharge of ions may also be considered in the light of their discharge potential. The ions which require the minimum potential i.e. the least energy for their discharge at the electrode will be liberated first and then the other ions in the said order. The following table shows a list of cations and anions arranged in order of their increasing tendency to be discharged at the cathode and anode respectively.

Cations :

$$K^+ < Ca^{+2} < Na^+ < Mg^{+2} < Al^{+3} < Zn^{+2} < Fe^{+2} < H^+ < Cu^{+2} < Ag^+ < Au^{-}$$

$\longrightarrow$

Increasing tendency to get discharged at the cathode

Anions : $SO_4^{--} < NO_3^- < Cl^- < Br^- < I^- < OH^-$

$\longrightarrow$

Increasing tendency to be discharged at the anode

Let us now exaplain the products of electrolysis in the light of the ionic theory taking some typical examples.

(1) *Electrolysis of water using platinum electrodes* : Water is a very weak electrolyte and dissociates slightly into H^+ and OH^- ions : $H_2O \rightleftharpoons H^+ + OH^-$. So water is a very feeble conductor of electricity. The conductivity of water is greatly increased if a little H_2SO_4 is added to it, which dissociates greatly yielding H^+ and SO_4^{--}ions. The electrolyte will then contain H^+, OH^- and SO_4^{--} ions.

$$H_2O \rightleftharpoons H^+ + OH^- ; \quad H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}.$$

During electrolysis using platinum electrode, the positively charge H^+ ions are discharged at the cathode yielding H atoms. Every two atoms unite to form hydrogen molecules which are evolved as gas at the cathode. Both the anions OH^- and $SO_4^{=}$ are attracted towards the anode. But OH^- ions are preferentially discharged at the anode forming OH radicals because it is easier for OH^- ions to be discharged on Pt-anode than SO_4^{--}

ions. The OH radicals then react with one another forming water with the evolution of oxygen at the anode.

At Cathode $H^+ + e = H$; $H + H = H_2$

At Anode $OH^- - e = OH$; $4OH = 2H_2O + O_2$.

That is electrolysis of dilute H_2SO_4 produces hydrogen and oxygen, in fact, water is electrolysed.

(2) *Electrolysis of NaOH Solution using platinum electrodes* :

In a dilute solution of caustic soda, Na^+, H^+ and OH^- ions are present ;

$$H_2O \rightleftharpoons H^+ + OH^- ;\ NaOH \rightleftharpoons Na^+ + OH^-$$

During electrolysis, OH^- ions move towards the anode, get discharged to produce OH radicals. which react evolving oxygen. Both the Na^+ and H^+ ions move towards the Pt-cathode, but the H^+ ions (and not Na^+ ions) are preferentially discharged at the cathode. Hence hydrogen gas is evolved at the cathode. Therefore electrolysis of dilute NaOH solution also gives hydrogen and oxygen at cathode and anode respectively. This is also, in fact the electrolysis of water.

At the cathode : $H^+ + e = H$; $H + H = H_2$

At the anode : $OH^- - e = OH$; $4OH = 2H_2O + O_2$

(3) *Electrolysis of sodium chloride solution* : In the aqueous solution of sodium chloride, the cations present are Na^+ and H^+, and the anions are Cl^- and OH^-. $H_2O \rightleftharpoons H^+ + OH^-$; $NaCl \rightleftharpoons Na^+ + Cl^-$. The product of electrolysis of such a solution depend upon the nature of the electrodes used.

(a) *With graphite electrodes* : When graphite electrodes are used, H^+ ions, and not the Na^+ ions, are preferentially discharged at the cathode and yield first atoms and then molecules of hydrogen which are liberated as gas. At the anode, between Cl^- and OH^- ions, the former are more easily discharged yielding chlorine atoms, because these are present in much greater concentration than OH^- ions. The chlorine atoms then combine in pairs to give molecules which is liberated as chlorine gas at the anode.

At the cathode : $H^+ + e = H$; $H + H = H_2$

At the anode : $Cl^- - e = Cl$; $Cl + Cl = Cl_2$

The solution after electrolysis, contains Na^+ and OH^- ions, i.e. caustic soda, NaOH.

(b) *With mercury cathode* : If mercury is used as cathode and graphite as anode, then chlorine gas will be produced as before at the anode. But at mercury cathode. Na^+ ions are more easily discharged than the H^+ ions. So Na^+ ions are discharged at the cathode and form an amalgam with mercury.

At the cathode ; $Na^+ + e = Na$; $Na + xHg = NaHg_x$.

(c) *With platinum electrodes* : If the solution of NaCl is dilute and pt-eletrodes are used, the products of eletrolysis will be hydrogen at the cathode and oxygen at the anode, just like electrolysis of water. Thus,—

At the cathode : $H^+ + e = H$; $H + H = H_2$

At the anode : $OH^- - e = OH$; $4OH = 2H_2O + O_2$

(4) *Electrolysis of copper sulphate solution* : Aqueous solution of copper sulphate yields Cu^{++} and H^+ ions as cations, and SO_4^{--} and OH^- ions as anions.

$H_2O \rightleftharpoons H^+ + OH^-$; $CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$.

Here also the products of electrolysis depends upon the nature of the electrodes.

(a) *With platinum electrodes* : Of the two cations present, Cu^{++} ions are preferentially discharged at the platinum cathode as it occupies lower position in the electrochemical series than hydrogen. The pt-cathode is thus coated with a deposit of copper. At the anode, OH^- ions are discharged in preference to SO_4^{--} ions, the OH groups then react to form water and oxygen which evolved as a gas.

At the cathode : $Cu^{++} + 2e = Cu$

At the anode : $OH^- - e = OH$; $4OH = 2H_2O + O_2$.

Due to the discharge of Cu^{++} ions, the blue colour of the electrolyte gradually fades away, the solution contains H^+ and SO_4^{--} ions, i.e., sulphuric acid after electrolysis.

(b) *With copper electrodes* : When copper electrodes are used cupric ions are dischraged as usual and metallic copper is deposited at the cathode in preference to hydrogen. But at the copper anode, neither OH^- nor SO_4^{--} ions are discharged but copper atoms from the anode are transformed into ions of copper and pass into solution ; in short the anode dissolves. This is because the electrons (negative charges) are removed more easily from a copper atom than from a SO_4^{--} or a OH^- ion to affect its discharge. Hence,

At the cathode : $Cu^{++} + 2e = Cu$;
At the anode : $Cu - 2e = Cu^{++}$.

So, during electrolysis of copper sulphate using copper electrodes, copper dissolves at the anode and deposits at the cathode, i.e mere transfer of copper from the anode to the cathode. The concentration of the electrolyte in the cell is maintained constant. Likewise, if silver nitrate is electrolysed between platinum electrodes, metallic silver deposits at the cathode and oxygen is evolved at the anode. But during electrolysis with silver electrodes, silver deposits at the cathode and an equal amount of silver dissolves from the anode. In fact, NO_3^- and SO_4^{--} ions are never discharged at the anodes from aqueous solutions.

N.B. From the discussions so far made, it is to be noted that all chemical reactions which occur at the anode and cathode during electrolysis are oxidation and reduction respectively, because the reaction occurring at the anode involves the removal of electron (s) and the that occuring at the cathode involves the gain of electron (s) by an ion.

12·6. **Ampere and Coulomb :** **Ampere** is the practical unit of current and is defined as the current which when passed for 1 second through silver nitrate solution, deposits 0·001118 gram of silver at the cathode.

Coulomb is the practical unit of the quantity of electricity. It is the quantity of electricity passing through a circuit in one second when 1 ampere of current flows. So if C amperes of current flow uniformly through a conductor for t seconds, the quantity of electricity Q in coulombs is given by $Q = C \times t$. i.e., Coulomb = ampere × second. A coulomb may also be defined as the quantity of electricity that liberates 0·001118 gram of silver or 0·0000104 gm. of hydrogen from appropriate solution at the cathode.

12·7. Faraday's Laws of Electrolysis :

Michael Faraday made extensive study of electrolysis and found that there is a quantitative relation between the quantity of electricity passing through an electrolyte and the amount of chemical change occuring at the electrodes. This quantitative relationship was enunciated by Faraday in the form of two laws in the year 1832 long before anything was known about the mechanism of the process of electrolysis. The two laws of Faraday are stated as follows—

(I) **First Law :** *The amount of chemical change (measured by ihe mass of substance deposited or dissolved) occuring at any electrode during electrolysis is strictly proportional to the quantity of electricity which passes through the electrolyte.*

If W gm of a substance is deposited or dissolved at an electrode when Q coulombs of electricity are passed, then

$$W \propto Q \quad \text{or,} \quad W = ZQ, \qquad (12.1)$$

Now, if a uniform current of C amperes flows for t seconds, then the quantity of electricity passed. $Q = C \times t$. Hence

$$W = Z \times C \times t \qquad (12.2)$$

Where Z is a constant characteristic of the element liberated and is called the *electro chemical equivalent* (E. C. E.)

When $Q = 1$ i, e., one coulomb of electricity (a current of 1 ampere for one second) passes, $W = Z$. Thus,

The *electrochemical equivalent* of an element is the mass in grams of the element which is liberated by the passage of unit quantity, i. e., 1 coulomb of electricity through the electrolyte.

It has been observed that 1 coulomb of electricity liberates 0·00118 gm. of silver from a solution of $AgNO_3$ or 0·0000104 gm.

of hydrogen from acidulated water. So E. C. E. of Ag is 0·001118, E.C.E of hydrogen is 0·0000104.

(2) **Second Law:** When the same quantity of electricity is passed through a number of different electrolytes, the amounts of the substances liberated at different electrodes are proportional to their chemical equivalents.

Let W_1 and W_2 gm of two substances are produced at two electrodes by the same quantity (Q coulombs) of electricity. Then,

$$\frac{W_1}{W_2}=\frac{E_1}{E_2}, \qquad \text{....12·3}$$

where E_1 and E_2 are their respective chemical equivalents (equivalent weights)

To illustrate: Several voltameters, containing acidulated water, solutions of HCl, $AgNO_3$ and $CuSO_4$, are connected in series so that same quantity of electricity passes through all of them.

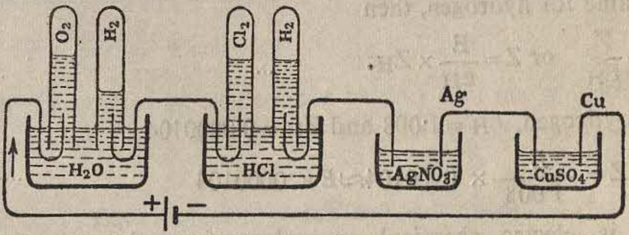


Fig. 12.3 Electrolysis of different substances

After electrolysis for some time, it is found that, when 1·008 gm. of hydrogen is evolved at one electrode, the quantities of other substances produced at other electrodes are 8 gm oxygen, 35·5 gm chlorine, 107·88 gm silver and 31·75 gm copper—these are their respective chemical equivalents (Fig 12.3).

12·8. Consequences of Faraday's Laws:

Three important consequences are followed from the two laws of Faraday when considered jointly.

1. From the 1st Law, we have

$W_1=Z_1Q$ and $W_2=Z_2Q$, where W_1 and W_2 are the weights of two substances liberated for the passage of the same quantity of electricity (i.e. Q coulombs); Z_1 and Z_2 are their electrochemical equivalents.

$$\therefore \quad \frac{W_1}{W_2}=\frac{Z_1}{Z_2}. \qquad \text{....} \qquad \text{...12·4}$$

Again from the 2nd Law, we have $\frac{W_1}{W_2}=\frac{E_1}{E_2}$

$$\text{Hence,} \quad \frac{E_1}{E_2}=\frac{Z_1}{Z_2}\text{ ; i.e., } E \propto Z. \qquad \text{....} \qquad \text{....12·5}$$

The chemical equivalent of an element is proportional to its electrochemical equivalent. That is,

$$\frac{\text{Electro chemical Equivalent of the element A}}{\text{Electro chemical Equivalent of the element B}}=\frac{\text{Chemical Equivalent of A}}{\text{Chemical Equivalent of B}}$$

2. If E and Z are the chemical equivalent and electrochemical equivalent of an element respectively and if E_H and Z_H are the same for hydrogen, then

$$\frac{E}{E_H}=\frac{7}{E_H} \quad \text{or } Z=\frac{E}{E_H}\times Z_H. \qquad \text{....} \qquad \text{....12·6}$$

for hydrogen, $E_H = 1·008$ and $Z_H = 0·0000104$

$$\therefore \quad Z=\frac{E}{1·008}\times ·0000104 \approx E\times ·0000104 \qquad \text{....(12·7)}$$

That is, electro chemical equivalent of an element = chemical equivalent of the element × 0·0000104 (approximately).

3. Combination of the two laws of Faraday lead to another interesting result.

From 1st Law: $W \propto Q$ when E (chemical equivalent) is constant.

From 2nd Law : $W \propto E$, when Q (electricity passed) is constant.

Combining the two, we have, $W \propto QE$, or $W=kQE$, ...(12.8)
when k is a constant and both Q and E vary independently

$\therefore \quad Q=\frac{1}{k}\times\frac{W}{E}$. Now, if $W=E$, i.e. if 1 gm equivalent weight of a substance be produced by electrolysis, we have, $Q=\frac{1}{k}$, that is, a definite quantity of electricity is required to deposit or dissolve 1 gram equivalent of any substance during electrolysis. This constant quantity of electricity which produces 1 gm equivalent of a substance by electrolysis is known as one **Faraday** of electricity and is denoted by F.

$\therefore \quad F=\frac{1}{k}$, substituting in equation, (12.8) we have,

$$W=\frac{QE}{F}=\frac{E\times C\times t}{F} \quad (\because \quad Q=C\times t) \qquad \text{....(12.9)}$$

Magnitude of F :

From equations (12.1) and, (12·9)

$W=ZQ$ and $W=\frac{QE}{F}$.

Hence $Z=\frac{E}{F}$ or, $F=\frac{E}{Z}$. (12.10)

F is a constant, it is the quantity of electricity that liberate 1 gr. equivalent of an element.

$$\therefore \quad F=\frac{E_1}{Z_1}=\frac{E_2}{Z_2}=\frac{E_3}{Z_3}.$$

Both E and Z of an element can be very accurately determined experimentally from which the value of F can be computed as follows .–

Element	Equv. wt. (E)	Electro chemical Equv. (Z)	$F=E/Z$ (coulombs)
Hydrogen ...	1·008	0·0000104	96496
Silver	107·88	0·001118	96495
Copper	31·78	0·0003294	96494
Oxygen	8·00	0·0000829	96495
			≈96500.

$\therefore$ one Faraday, $F=96500$ coulombs (approximately).

Hence equation, (12.9) may be expressed as $W=\frac{ECt}{96500}$ (12.11

12·9. Determination of Equivalent weight by electrochemical method.

For this purpose the following relations which follow from Faraday's laws are used :

(i) $Z = E \times 0{\cdot}0000104/1{\cdot}008$; (ii) $W = ECt/F$; (iii) $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

(a) *Determination of equivalent weight of silver* :—

A platinum basin is carefully cleaned, dried and weighed. An aqueous solution of $AgNO_3$ (approx. 15%) is taken in the basin which serves as both the cathode as well as the electrolytic cell. In this solution is suspended from above a thin pure silver wire (Fig. 12-4). The basin is now connected to the negative terminal of a battery. The silver wire is connected to the positive terminal of the battery through a sensitive milliammeter for measuring the current and an adjustable resistance. The circuit is closed and the current is passed for a difinite time (known from a stop-watch). Due to the passage of electricity, silver is deposited on the Pt-basin which is the cathode. After switching off the current, the solution is then decanted and the basin containing the silver deposit is washed repeatedly with distilled water, finally dried and weighed. The increase in weight gives the weight (W) of silver deposited. The amount of current passed is read from the milliammeter. Since W, C and t are all known, Z, the electrochemical equivalent of silver is first determined from the equation $W = ZCt$ (1st Law) or $Z = W/ct$. Then E. the equivalent weight of silver is calculated from the relations :

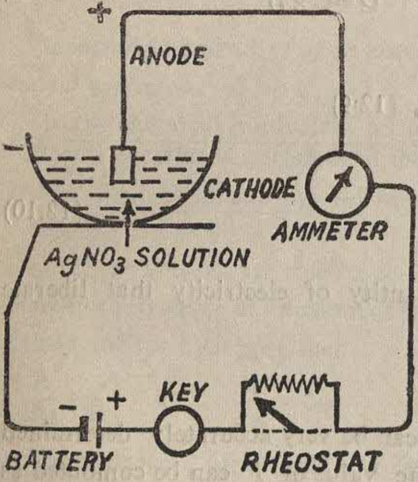


Fig. 12.4 Detn. of eq. wt. of silver

(i) $E = Z \times 1{\cdot}008/0{\cdot}0000104$; (ii) $E = W \times 96500/Ct$.

From actual experiment, the value of the equivalent weight of silver is found to be 107·88.

(b) *Determination of equivalent weight of copper* :—

Two electrolytic cells, one containing copper sulphate solution and the other silver nitrate solution, are connected in series through an adjustable resistance and milliammeter. The same current is then passed through the two cells for same time and the weights of silver and copper deposited on the respective cathodes are determined accurately after electrolysis. Then by the 2nd law of Faraday : $\frac{W_1}{W_2}=\frac{E_1}{E_2}$, where W_1 and W_2 are the weights of copper and silver, and E_1 and E_2 are their respective equivalents. Taking the equivalent weight of silver to be 107·88, that of copper can be calculated from the above equation.

Indeed, the electrochemical method for determination of chemical equivalent is a very accurate one.

12·10. **Significance of Faraday's Laws** : **Unit of electricity :**

From Faraday's Law, it is found that 1 gm equivalent of an ion carries 1 Faraday i.e., 96500 coulombs of electricity. Therefore the quantity of electricity carried by 1 gm ion of valency $n=nF$ coulombs, since,

1 gm ion of any ion is numerically equal to 1 gram-atom which is equal to gram equivalent × valency.

Again, the number of individual ions in 1 gram ion is equal to the Avogadro's number $N=6{\cdot}023\times10^{23}$.

$\therefore$ the quantity of electrictity carried by a single ion $=\frac{nF}{N}$.

Since n is an integer, being 1 for univalent ion, 2 for bivalent ion and so on, the amount of electricity carried by a single ion is a multiple of a minimum quantity of electricity F/N. which may thus be regarded as the fundamental unit of electricity. In other words, *electricity like matter, is atomic in nature* and the value of the atom of electricity is $\frac{F}{N}$.

Thus the unit (or atom) of electricity $=\frac{F}{N}$

$$=\frac{96500\text{ coulombs}}{6{\cdot}023\times10^{23}}=1{\cdot}6\times10^{-19}\text{ coulombs}$$

This unit of electric charge F/N has been identified with the charge of an electron, the unit negative charge, e.

$\therefore \quad e = F/N = 1{\cdot}6 \times 10^{-19}$ coulombs.

or, $F = Ne$. .... (12.12)

So a Faraday contains the same number of unit charges as the number of molecules in a mole. Hence, a *Faraday* (F) may be called a *mole of electricity*.

The charge carried by any ion of valency 'n' is therefore, given by $ne = n \times 1{\cdot}6 \times 10^{-19}$ coulombs.

Again equation, (12.12) may be written as $N = \frac{F}{e}$. ... (12.13)

The value of F is known to be 96500 coulombs ; e, the electronic charge has been independently determined by Millikan. The relation $N = F/e$, thus, provides an excellent method of finding the value of Avogadro's number from the experimental value of F and e.

N.B. (1) The most remarkable feature of Faraday's Laws is the simplicity which made the study of electrolysis very easy. According to these laws, the amount of electrolysis depends only on the quantity of electricity passed through the electrolyte and on nothing else.

(2) Since the Faraday's law is very exact and rigidly obeyed, it is used for measuring the quantity of electricity passing through an electric circuit by means of an electrolytic cell.

(3) These laws also contained the seed of the concept of atom of electricity i.e., the electron.

12·11. Electrolytic dissociation and thermal dissociation :

When ammonium chloride is dissolved in water, the molecules split up partly into NH_4^+ and Cl^- ions in solution and these ions also reunite to form undissociated NH_4Cl molecules. This is electrolytic dissociation.

But when ammonium chloride is heated, it partly breaks up into NH_3 and HCl molecules which however unite when cooled. This is thermal dissociation.

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$; (electrolytic dissociation)

$NH_4Cl \rightleftharpoons NH_3 + HCl$; (thermal dissociation)

The thermal dissociation differs from electrolytic dissociation in the following respects :

(1) Both thermal and electrolytic dissociations are reversible, i.e., proceed in both directions. But the products of thermal dissociation are neutral atoms or molecules, while those of electrolytic dissociation are electrically charged atoms or radicals, called ions.

(2) The products of thermal dissociation are separable by easy physical means, such as solution, diffusion etc. But products of electrolytic dissociation cannot be separated easily owing to the electrostatic attraction between them.

(3) In thermal dissociation no medium is necessary, while in electrolytic dissociation, the electrolyte is dissolved in an ionising solvent or is fused.

(4) Both thermal and electrolytic dissociation depend on temperature, but the influence of temperatue on electrolytic dissociation is relatively less.

12·12. **Technical application of electrolysis** :

The processes of electrolysis are taken advantage of in purification of metals, in electroplating, electrotyping, electrometallurgy etc.

Electrorefining : Metals like copper, silver, lead etc. when extracted from respective ores are somewhat impure. By means of electrolytic process the impure metal may be purified. Take for example, to purify copper, the impure copper blocks are used as anode and strips of pure copper are used as cathode with copper sulphate solution as electrolyte. On electrolysis, copper ions are selectively deposited at the cathode while the copper at the anode goes into solution and the impurities fall off as a slime. Pure silver, lead, zinc etc. are also obtained by similar electrorefining.

Electroplating : In electroplating a thin but coherent layer of a metal like nickel, copper, chromium, gold etc. is deposited electrically on the surface of a cheaper article to prevent their corrosion and sometimes to add to their commercial value. In silver plating, the article is thoroughly cleaned and suspended in a bath of potasssium argento-cyanide [$KAg(CN)_2$] solution as cathode. The electrolytic bath is prepared by adding excess of potassium cyanide to silver nitrate solution. A pure silver plate is used as the anode and suspended in the same solution. If the article is a non conductor, it is first covered with a thin layer of graphite. On passing current, a uniform deposit of silver takes place on the article at the cathode. Electroplating with gold, nickel, copper etc. are also carried out in the same way.

Electrotyping : The types used in printing are also prepared through electrodeposition. At first an impression of the ordinary types is made on wax which act as the cast. Its surface is dusted with graphite powder to make it conducting. This surface is copper plated by making it the cathode in an electrolytic cell, where the anode is pure copper and the electrolyte copper sulphate solution. When a thick plate has been formed, it is detached from wax by melting off the latter, Printing is then done from the copper plate. The same principle is also used to make metal-statues, busts etc.

Electrometallurgy : Different metals like sodium, magnesium, calcium, aluminium, copper etc. (also some non-metals) are often commercially prepared by electrolytic method. For example, Metallic alumintum is almost exclusively produced by electrolysis of pure alumina dissolved in fused cryolite.

12.13. The Electrochemical series :

The metals and hydrogen are electropositive and they have a tendency to give positive ions by losing electrons ;

$Cu = Cu^{++} + 2e$; $\frac{1}{2}H_2 = H^+ + e$; $Na = Na^+ + e$ etc.

When a metal strip or rod is dipped partially into an aqueous solution containing its own ions, a few metal ions would pass into the solution leaving behind an excess of electrons on the metal surface. So the metal surface acquires a negative charge which attracts the positive ions of the solution. As a result an 'electrical double layer' of two opposite charges is formed in the immediate vicinity of the metal surface (Fig. 12.5). This double layer leads to a difference of potential between the metal surface and the solution layer in its immediate contact. This is known as the electrode potential of the metal, which also depends upon the concentration of its ions in the surrounding solution.

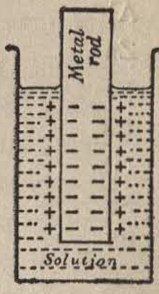


Fig. 12.5 The double layer

The electrode potential is a measure of the tendency of the metal to from ions. Different metals possess different electrode potentials indicating that the tendency of the metal to lose electrons and to go into solution as metallic ions is different for differnt metals. When a metal or an element is placed in contact with a solution containing its own ions having concentration 1 gm-ion/litre, the potential developed is called the standrad electrode potential ; the temperature is kept at 25°C. We shall see later that the tendency of a substance to lose one or more electrons is known as oxidation. Hence the electrode potential so developed is called standard oxidation potential, so that they correspond to the process $M \rightarrow M^{+x} + xe$. The higher the oxidation potential of the metal, the greater is its tendency to ionise and so possesses greater reducing power.

The metals have been arranged in a descending order of their standard oxidation potentials and the list so formed called "the electrochemical series", which is shown in the following table.

The Electro chemical Series

Element	*Mode of Oxidation*	*Standard oxidation*
Metals		*potential* (*Volt*) *at* 25°C
Li	$Li \rightarrow Li^+ + e$	+3·05
K	$K \rightarrow K^+ + e$	+2·93
Ca	$Ca \rightarrow Ca^{++} + 2e$	+2·87
Na	$Na \rightarrow Na^+ + e$	+2·71
Mg	$Mg \rightarrow Mg^{++} + 2e$	+2·37

Element Metal	*Mode of oxidation*	*Standard oxidation potential (Vol.) at 25°C*
Al	$Al \rightarrow Al^{+++} + 3e$	+1·66
Zn	$Zn \rightarrow Zn^{++} + 2e$	+0·76
Fe	$Fe \rightarrow Fe^{++} + 2e$	+0·44
Cd	$Cd \rightarrow Cd^{++} + 2e$	+0·40
Ni	$Ni \rightarrow Ni^{++} + 2e$	+0·25
Sn	$Sn \rightarrow Sn^{++} + 2e$	+0·14
Pb	$Pb \rightarrow Pb^{++} \rightarrow 2e$	+0·13
H	$H \rightarrow H^{+} + e$	0 00
Cu	$Cu \rightarrow Cu^{++} + 2e$	−0·34
Hg	$Hg \rightarrow Hg^{++} + 2e$	−0 79
Ag	$Ag \rightarrow Ag^{+} + e$	−0·80
Au	$Au \rightarrow Au^{+++} + 3e$	−1·50

The non-metals also have such standard electrode potentials and they can be arranged in a descending order of their standard oxidation potentials. In these cases the oxidation process is represented by $A^{-} — A + xe$; i.e. the non-metallic ions will be converted into the non-metals by losing one or more electrons. The standard oxidation potentials of some non-metals are given below :—

Element non-metal	*Mode of oxidation*	*Standard oxidation potential (volt) at 25°C*
Oxygen	$(OH)^{-} \rightarrow \frac{1}{2}O_2 + e$	−0·40
Sulphur	$S^{--} \rightarrow S + 2e$	−0·51
Iodine	$I^{-} \rightarrow \frac{1}{2}I_2 + e$	−0·53
Bromine	$Br^{-} \rightarrow \frac{1}{2}Br_2 + e$	−1·07
Chlorine	$Cl^{-} \rightarrow \frac{1}{2}Cl_2 + e$	−1·36

The electro chemical series serves as a very useful guide to decide the relative chemical reactivities of the elements and their compounds. This is illustrated below.

(1) *Electro positive character* ; The elements at the top of the series are most electropositive and this character diminishes as we go down the series. So the metals occupying the higher

position will have greater tendency to lose electrons and will behave as a stronger reducing agent than the metal in the lower position. Thus, aluminium is a stronger reducing agent than iron.

(2) *Discharge of ions at the electrodes* : If an electrolyte contains a number of different ionic species (both cations and anions), then each ionic discharge will occur as the appropriate potential is reached. Since the metals and hydrogen are liberated at the cathode, the process at the cathode involves the taking up of electrons i.e. reduction in the most general sense. Cathodic process will therefore take place in the order of decreasing reduction potential, that is, in the order of increasing oxidation potentials of the metals. Hence, lower the position of the metal in the electro chemical series, the greater is the tendency to be liberated at the cathode. Thus Cd^{++} ions are discharged in preference to the Zn^{++} ions. Similarly the anions are liberated at the anode by giving up electrons and so the process at the anode is nothing but oxidation. So the anodic process will occur in the order of decreasing oxidation potentials of the non-metals. Thus the Br^- ions will be discharged in preference to the Cl^- ions.

(3) *Displacement of metals* : A metal will be displaced from its salt solution by any metal occupying a higher position in the electro chemical series. Thus, iron displaces copper from copper sulphate solution, sodium displaces aluminium from aluminium chloride.

$Fe + CuSO_4 = FeSO_4 + Cu$; $3Na + AlCl_3 = 3NaCl + Al$.

Conversely, in the case of non-metals, a non-metal lower in the series will displace a non-metal higher in the series (i. e. less electro negative one) Thus

$Cl_2 + 2KBr = Br_2 + 2KCl$; $Br_2 + 2KI = I_2 + 2KBr$.

(4) *Displacement of hydrogen from water and acids* : Metals above hydrogen (with the exception of lead), displace hydrogen from dilute acids (HCl, H_2SO_4 etc.). The metals below hydrogen do not release hydrogen from these acids.

All metals above hydrogen except lead and tin, are capable of displacing hydrogen from water. The higher the metal in the series, the more vigorous is the reaction with water. Metals (below hydrogen in the series), like Cu, Ag, etc. do not displace hydrogen directly from water.

$$Mg+2HCl=MgCl_2+H_2\ ; \quad Fe+H_2SO_4=FeSO_4+H_2$$

$$2Na+2H_2O\xrightarrow{\text{cold}}2NaOH+H_2\ ; \quad Mg+2H_2O\xrightarrow{\text{heat}}Mg(OH)_2+H_2$$

$$3Fe+4H_2O\xrightarrow{\text{steam}}Fe_3O_4+4H_2.$$

(5) *Reaction with oxygen*; The affinity towards oxygen systematically decreases in passing down the series. In consequence, the stability of the metallic oxides increases with the increasing electro-positiveness of the metal. For example, the oxides of metals above and upto aluminium are too stable to be reduced by carbon (with the exception of magnesium). The oxides of metals below aluminium are reduced by carbon with increasing ease with decreasing electropositiveness of the metals. The stability of oxides of mercury, silver and gold is so low that they are decomposed by heat alone.

$$Fe_2O_3+3C=2Fe+3CO\ ; \quad 2Ag_2O\xrightarrow{\text{heat}}4Ag+O_2.$$

(6) *Oxy salts*: The stability of the oxysalts of the metals such as carbonates, nitrates, etc. decrease systematically in passing down the electrochemical series.

$$CaCO_3\xrightarrow{\text{at }800°C}CaO+CO_2$$

$$PbCO_3\xrightarrow{\text{at }350°C}PbO+CO_2$$

$$CuCO_3\xrightarrow{\text{at }100°C}CuO+CO_2$$

(7) It has been seen that the chemical reactivity of the metals decreases as we go down the series. This is why the metals occupying higher position occur in the combined state. whereas Cu, Ag, Hg etc. are often found in the elementary state. In the case of non-metals, it would be the reverse:

Numerical Problems :

1. What will be the electrochemical equivalent of oxygen if that of silver be 0·001118 ? (The eqv. wt. of Ag = 107·8)

we know, $\frac{\text{E.C.E. of } O_2}{\text{E.C.E. of Ag}} = \frac{\text{C.E. of } O_2}{\text{C.E. of Ag}}$

i.e. $\text{E.C.E. of } O_2 = \frac{8}{107 \cdot 8} \times 0 \cdot 001118 = 0 \cdot 0000829.$

2. A current of 0·5 ampere is sent through a solution of copper sulphate for 20 minutes using platinum electrodes. Calculate (i) the weight of copper deposited at the cathode, (ii) number of copper atoms deposited and (iii) volume of oxygen liberated at the anode at N.T.P.

(Eqv. wt. of copper = 31·78)

(i) From the relation $W = \frac{E \times C \times t}{96500}$, weight of copper deposited

$$= \frac{0 \cdot 5 \times 20 \times 60}{96500} \times 31 \cdot 78 = 0 \cdot 1976 \text{ gm},$$

(ii) 1 gm. atom, i.e., 63·56 gm of copper contain $6 \cdot 023 \times 10^{23}$ atoms.

∴ 0·1976 gm. of copper contain $\frac{6 \cdot 023 \times 10^{23} \times 0 \cdot 1976}{63 \cdot 56}$

$$= 0 \cdot 1873 \times 10^{22} \text{ atoms.}$$

(iii) wt. of oxygen liberated $= \frac{8 \times 0 \cdot 5 \times 20 \times 60}{96500} = 0 \cdot 0497$ gm.

and its volume at N.T.P. $= 0 \cdot 0497 \times 22400/32 = 34 \cdot 79$ cc.

3, (a) What current strength in amperes will be required to liberate 5 gms of iodine from a potassium iodide solution in 30 minutes ? (I = 127).

$$W = \frac{ECt}{96500} \text{ or, } C = \frac{W \times 96500}{E \times t} = \frac{5 \times 96500}{127 \times 30 \times 60} = 2 \cdot 11 \text{ amp.}$$

(b` Calculate the number of electrons passing per second through any point on a metallic copper wire, when a current of 0·4825 ampere flows through it.

The charge of an electron $= \frac{F}{N} = \frac{96500}{6 \cdot 02 \times 10^{23}} = 1 \cdot 6 \times 10^{-19}$ coulomb.

i.e. $1{\cdot}6 \times 10^{-19}$ ampere per second is carried by 1 electron.

$\therefore$ 0·4825 ampere per second is carried by $\dfrac{1 \times {\cdot}4825}{1{\cdot}6 \times 10^{-19}}$

$= 3{\cdot}01 \times 10^{18}$ electrons

4. The same current is passed through acidulated water and through a solution of the chloride of metal X. The volume of hydrogen liberated at N.T.P. was 14·8 litres and the weight of the metal deposited 42 gm. The specific heat of the metal is 0·094. Find the formula of the chloride.

The approximate at. wt. of the metal $= \dfrac{6{\cdot}3}{0{\cdot}094} = 67{\cdot}02$

The hydrogen liberated at N.T.P. $= 14{\cdot}8$ litres $= \dfrac{14{\cdot}8}{11{\cdot}2}$equivalents

Hence the metal deposited must also be $\dfrac{14{\cdot}8}{11{\cdot}8}$ equivalents

or, $\dfrac{14{\cdot}8}{11{\cdot}2}$ equivalents of the metal $= 42$

$\therefore$ 1 equivalent of the metal $= \dfrac{42 \times 11{\cdot}2}{14{\cdot}8} = 31{\cdot}78.$

Hence the valency of the metal $= \dfrac{67{\cdot}02}{31{\cdot}78} = 2{\cdot}108 \approx 2.$

$\therefore$ the formula of the chloride is XCl_2

5. Calculate the weight of water which on electrolysis would give sufficient hydrogen at 15°C and 760 mm. to fill up a balloon of one million litres capacity.

1 million litres of hydrogen at 15°C and 760 mm. will occupy $\dfrac{273}{288} \times 10^6$ lit at N.T.P.

Now on electrolysis, 18 gm. of water produces 2 gm of hydrogen = 22·4 litres of H_2 at N. T. P.

$\therefore$ Weight of water required to literate $\frac{273}{288} \times 10^6$ litres of hydrogen $= \dfrac{18 \times 273 \times 10^6}{22{\cdot}4 \times 288} = 7{\cdot}6 \times 10^5$ gms.

6. The cost of electricity for producing 1 kg of silver from silver nitrate is Rs 2·00. Find the cost of electricity for producing 18 kg of magnesium from magnesium chloride (Ag = 108, Mg = 24).

1000 gm of Ag = 1000/108 gm. eqv. of Ag.

18000 gm Mg = 18000/12 gm. eqv. of Mg.

The cost of producing 1000 gm of Ag is Rs 2·00

i.e., the cost of producing 1000/108 gm. eqv. Ag is Rs 2·00, Hence by second law of Faraday,

the cost of producing 1000/108 gm. eqv. of Mg Rs 2·00.

∴ the cost of producing 18000/12 gm eqv. of

$$\text{Mg} = \frac{2 \times 108}{1000} \times \frac{18000}{12} = \text{Rs. } 324{\cdot}00$$

7. 0·295 gm copper was deposited from a solution of copper sulphate when 0·25 ampere was passed for an hour. What is the equivalent weight of copper ?

$$W = \frac{\text{Ect}}{96500} \text{ or, } E = \frac{W \times 96500}{\text{C} \times \text{t}} = \frac{{\cdot}295 \times 96500}{{\cdot}25 \times 60 \times 60} = 31{\cdot}6$$

8. A current was passed through $AgNO_3$ solution and then through a gold salt solution. It was found that 1·9223 gms of Ag were deposited in the same time as 3·5128 gms of Au. If gold is monovalent, what is its atomic weight ? (equivalent weight of Ag is 108).

$$\text{From 2nd law, } \frac{\text{wt. of Ag}}{\text{wt. of Au}} = \frac{\text{C. E of Ag}}{\text{C. E. of Au}}$$

$$\text{or, } \frac{1{\cdot}9223}{3{\cdot}5128} = \frac{108}{\text{C. E. of Au}}.$$

$$\therefore \text{ C. E. of Au} = \frac{108 \times 3{\cdot}5128}{1{\cdot}9223} = 197{\cdot}3$$

∴ the atomic wt. of Au = C. E. × valency

$$= 197{\cdot}3 \times 1 = 197{\cdot}3$$

Exercise—12

1. What is meant by electrolytic dissociation ? How does it differ from thermal dissociation ? State and explain the postulates of Arrhenius theory of electrolytic dissociation.

2. Explain the mechanism of conduction of electricity through the solution of an electrolyte.

Sodium sulphate solution coloured purple with litmus solution is electrolysed in a U-tube. Explain the colour changes around the electrodes.

3. Distinguish between,—(a) an atom and an ion; (b) electrolytes and nonelectrolytes. (c) Faraday and coulomb; (d) Strong electrolyte and weak electrolyte; (e) electronic and electrolytic conductors, (f) anode and cathode.

4. Explain and illustrate what you understand by elcctrolysis. State and explain Faradays laws of electrolysis and express them in the form of an equation. How would you determine the equivalent weight of copper eletro-chemically ?

5. (a) What is electrochemical equivalent of an element ? How is it related to its chemical equivalent ? What meaning does the statement : "the E.C.E. of silver is 0·001118" convey ?

6. (a) Explain the significance of Faraday's laws of electr lysis. Given the value of Avogadro's number N, how can you determine the electronic change.

(b) Show that electricity like matter particles is also discret in nature and the value of the elementary quantity of electricity is $1{\cdot}6 \times 10^{-19}$ coulomb.

(c) What is the charge carried by each of the following ions : (i) Na^+; (ii) Ca^{++}; (iii) Al^{+++}; (iv) SO_4^{--}.

7. (a) Exaplain "the electrochemical series". Cite at least three instances where it serves as a guide to study the chemical properties of metals.

(b) State at least three important technical applications of the phenomenon of electrolysis.

(c) Describe the principle of electro-separation of metals. How does it differ from the electro-refining of metals ?

8. Explain why :

(a) Same products are obtained when dil NaOH and did H_2SO_4 are electrolysed with pt-electrodes.

(b) Iron deposits copper from copper sulphate solution.

(c) An aqueous solutions of common salt can conduct electric current but that of cane sugan cannot,

(d) Sodium is not doposited at the pt-cathode when a solution of sodium chloride is electrolysed.

9. An electric Current is passed through—

(a) $CuSO_4$ solution using Cu-electrodes,

(b) NaCl solution using graphite electrodes,

(c) acidulated water using pt-electrodes.

What substances and in what quantities will be liberated at the electrodes in each case when I Faraday of electricity is passed through each solution ?

10. Calculate the value of (a) electrochemical equivalent of silver and (b) Faraday from the following data :

A current of 6 amperes in passed through a silver nitrate solution for 10 minutes when 4·028 gm. of silver is deposited. (Ag=108).

[(a) 0·00118 ; (b)96521 coulombs].

11. A current of 5 amperes is passed through a copper voltameter and a silver voltameter connected in series for 32 minutes and 10 seconds. Calculate the amount of Cu and Ag deposited. Given E.C.E. of Cu=0·000325 and of Ag=0·001118. [Ag=10·79 gm ; Cu=3·137 gm].

12. The same amount of electricity which liberated 100 c.c. of oxygen collected over water at 15°C and 750 mm of mercury, doposited 1·772 gm of silver. Calculate the equivalent of silver. (given—1 c.c. oxygen at N.T.P weighs 0·001429 gm, aqueous tension at 15°C=13 mm.) [107·9]

13. (a) When the same current was passed through a $Ag\ NO_3$ solution and a $CuSO_4$ solution, 0·106 gm copper and 0·3597 gm silver were deposited in their respective cathodes. What is equivalent weight of silver if that of copper be 31·8 ?

(b) How much silver will be deposited if 1·05 amp. be passed through $Ag\ NO_3$ solutation for 20 minutes ? [(a) 107·9, (b) 1·409 gm].

14. When the same quantity of current was passed through acidulated water and an aqueous solution of a sulphate of a metal in the same circuit, the hydrogen liberated was 9·87 litres (N.T.P.) and the metal doposited was 28 gms. The specfic heat of the metal is 0·093. Find the the formula of the sulphate. [MSO_4]

15. The charge a Cl^- ion is $1{\cdot}6\times10^{19}$ coulmb. Find out the Avogadro's number. [$6{\cdot}023\times10^{23}$]

16. What current should be supplied as to produce 9·20 gm. of sodium metal per hour from molten sodium chloride ? [10·72 amp.]

17. The atomic weight of a metal is 112. A solution of its chloride when electrolysed for 2½ hrs by passing 0·15 amp. produced 0·783 gm of the metal. What is the valency of the metal ? [2]

18. A current of 1·50 ampere was passed through 4 litres of 1·2M $CuSO_4$ solution for 2 hours. Calculate the weight of the products liberated at pt-electrodes and the strength of the acid formed in terms of normality. [Cu=3·536 gm, O_2=0·895 gm, acid=0·028 (N)]

[Hint : quantity of electricity pessed=10800 coulombs.

96500 coulombs produce 1 gr. eg. of H^+ ions.

$\therefore$ 10800 coulombs produce $\frac{10800}{95500}=0{\cdot}112$ gm, eg. of H^+ ions in solution.

Strength of 1 lit. solution containing 1 gm. equv. H^+ ion=1 (N)

$\therefore$ the req. strength$=\frac{1\times0{\cdot}112}{4}=0{\cdot}028$ (N)

19. Tha passage of a uniform current through dilute sulphuric acid with pt. electrodes for half an hour liberated 336 cc. of electrolytic gas (mixed hydrogen and oxygen) at N.T.P. Calculate the strength of the current. [1·072 amp.]

20. A current of 0·75 ampere is passed through a solution of a salt of metal for 45 minutes. Increase in the weight of the cathode is 0·6662 gm. Calculate the equivalent weight of the metal. [31.74].

21. How many H^+ ions and Cu^{++} ions are transformed into the respective atoms by passing a current of 1 ampere for 1 minute? $(N=6{\cdot}02\times10^{23})$ $[3{\cdot}74\times10^{20}\ ;\ 1{\cdot}87\times10^{20}]$

22. How many coulombs of electricity would be required to deposit 1000 gms of copper from a Cu-salt solution? (63·5) [3028457 coulomb]

CHAPTER—XIII

ACIDS, BASES AND SALTS

These are three distinct classes of compounds, to which most of the substances belong. Attempts were made to distinguish these compounds by giving suitable definitions for them. But the older concepts of Boyle, Lavoisier and others regarding these compounds are not precise. These compounds have been distinguished properly in the light of Arrhenius' theory of electrolytic dissociation (See chapter 12).

13·1. Acids : An acid is a compound containing one or more replaceable hydrogen atoms. According to Arrhenius's theory, an acid dissociates in aqueous solution giving H^+ ions. Thus, the compounds HCl, HNO_3, H_2SO_4, CH_3COOH are all acids since they undergo dissociation in aqueous solution producing H^+ ions.

$HCl \rightleftharpoons H^+ + Cl^-$: $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$:

$HNO_3 \rightleftharpoons H^+ + NO_3^-$: $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$.

Mere presence of hydrogen in the molecule of the compound will not make it an acid, e.g, C_6H_6, NH_3, CH_4 etc. are not acids, since they do not produce H^+ ions in aqueous solutions, All the hydrogen atoms present in the molecule of an acid may not be replaceable or ionisable. Thus in acetic acid only one of the four hydrogen atoms of the molecule ionises.

It is found that certain properties are shared by all acids. For example ;

(1) Acids react with metals like Zn, Mg, Al etc., which are more electro-positive than hydrogen (i.e. metals which are placed above hydrogen in the electro chemical series to produce salts and hydrogen.

acids		metal	salt
H_2SO_4	+	Zn	$= ZnSO_4 + H_2$
2HCl	+	Mg	$= MgCl_2 + H_2$

(ii) Acids always react with bases (i.e, metallic oxides and hydroxides) to form salts and water. Such reactions are called "acid-base" reactions.

acids		bases		salts		water
HNO_3	+	KOH	=	KNO_3	+	H_2O
H_2SO_4	+	ZnO	=	$ZnSO_4$	+	H_2O
$2HCl$	+	$Ca(OH)_2$	=	$CaCl_2$	+	$2H_2O$

(iii) Acids react with metallic carbonates and bicarbonates to form carbon dioxide in addition to salt and water :

$$HCl + NaHCO_3 = NaCl + H_2O + CO_2$$

$$H_2SO_4 + K_2CO_3 = K_2SO_4 + H_2O + CO_2$$

(iv) Acids, in aqueous solution turn the colour of the indicator blue litmus to red and have a sour taste.

Considering all the above criteria, an acid may be defined as follows :

Acids are compounds which contain hydrogen atoms replaceable partly or wholly by metal atoms or metal like radicals, dissociate in aqueous solution producing H^+ ions, react vigorously with bases to form salts and water, turn blue litmus red and are generally sour to taste.

N. B. H^+ ion or the bare proton does not exist as such in aqueous solution , it forms hydronium ion, H_3O^+ with water : $H^+ + H_2O \rightleftharpoons H_3O^+$.

13·2. Classification of acids :

1. Acids are generally divided into two classes : (a) Hydracids. and (b) Oxyacids.

(a) *Hydracids* are those which contain hydrogen and another non-metallic element (or radical) but do not contain oxygen. They take the suffix *i.c.* and the prefix-*hydro* in their names, e.g. hydrofluoric acid (HF), hydrochloric acid (HCl), hydroiodic acid (HI), hydro-cyanic acid (HCN), etc.

(b) *Oxy acids* contain oxygen as an essential element in addition to hydrogen and another non-metallic element , e.g. sulphuric acid (H_2SO_4), nitric acid (HNO_3), boric acid (H_3BO_3) etc.

In naming oxy acids, some conventions are followed. The ending *– ous* or *– ic* are used to denote acids containing smaller or larger proportions of oxygen respectively. If an element forms a series of oxyacids, the prefixes *hypo –* and *per –* are added to the names of the acids containing less oxygen than the *– ous* acid and more oxygen than the *– ic* acid respectively.

Acid producing element	Oxy-acids			
	Hypo-acid	– ous acid	– ic acid	per-acid
Nitrogen	$H_2N_2O_2$ hypo-nitrous	HNO_2 nitrous	HNO_3 nitric	HNO_4 per-nitric
Sulphur	$H_2S_2O_4$ hypo-sulphurous	H_2SO_3 sulphurous	H_2SO_4 sulphuric	$H_2S_2O_8$ per-sulphuric
chlorine	HOCl hypo-chlorous	$HClO_2$ chlorous	$HClO_3$ chloric	$HClO_4$ per-chloric
iodine	HOI hypo iodous	HIO_2 iodous	HIO_3 iodic	HIO_4 per iodic
phosphorus	H_3PO_3 hypo-phophorus	H_3PO_3 phosphorus	H_3PO_4 phosphoric	

In some cases, the oxygen of an oxy-acid may be replaced by sulphur, partially or completely, producing what are called *Thioacids*, e.g.,

Sulphuric acid H_2SO_4, Thiosulphuric acid $H_2S_2O_3$

Cyanic-acid HCNO, Thiocyanic acid HCNS.

2. Acids may also be classified according to their, basicities. Basicity of an acid is its power of neutralising a base and is expressed by the number of hydrogen ions produced from each molecule in aqueous solution. Thus hydrochloric acid, nitric acid, acetic acid are *monobasic*. Sulphuric acid, carbonic acid are *dibasic*. Phosphoric acid is *tribasic*. In general, acids containing more than one replaceable hydrogen atom are called *polybasic* acids.

Monobasic acid	**Dibasic acid**	**Tribasic acid**
$HCl \rightarrow H^+ + Cl^-$	$H_2SO_4 \rightarrow 2H^+ + SO_4^{--}$	$H_3PO_4 \rightarrow 3H^+ + PO^{3-}_4$
$HNO_3 \rightarrow H^+ + NO_3^-$	$H_2CO_3 \rightarrow 2H^+ + CO_3^{-}$	
$CH_3COOH \rightarrow H^+ + CH_3COO^-$		

3. Depending upon their strength, acids are divided mainly into two classes ; (a) Strong acids, (b) weak acids. As an acid produces H^+-ions in aqueous solution, the concentration of H^+ ions formed by the ionisation of an acid may be taken as measure of its stregth.

(*a*) *Strong acids* are those which are practically completly dissociated in aqueous solution producing large concentration of H^+-ions i.e., their degree of dissociation is very high. Examples are,— HCl, HNO_3, H_2SO_4 etc.

(b) *Weak acids* undergo only a partial dissociation in aqueous solution producing small concentration of H^+ ions, e.g., CH_3COOH, H_3BO_3, H_2CO_3 etc.

4. Acids are also classified into *mineral acids* and *organic acids*. Acids obtained from mineral source are known as "*mineral acids*" e.g., hydrochloric acid (from rock salt, NaCl), nitric acid (from saltpetre), phosphoric acid (from calcium phosphate) etc. The acids which contain carbon as an essential element and often obtained from living source are termed "*organic acids*", such as, tartaric acid (from grapes), citric acid (from lemons), etc.

13·3. Bases :—

Bases are compounds usually the oxides and hydroxides of metals or metal-like radicals and they react readily with acids forming salts and water. Examples are ;—

Na_2O, CaO, ZnO, CuO, etc NH_4OH, NaOH, $Ca(OH)_2$, $Al(OH)_3$ etc.

base		acid		salt		water
CaO	+	2HCl	=	$CaCl_2$	+	H_2O
CuO	+	H_2SO_4	=	$CuSO_4$	+	H_2O
NH_4OH	+	HCl	=	NH_4Cl	+	H_2O
$Ca(OH)_2$	+	$2HNO_3$	=	$Ca(NO_3)_2$	+	$2H_2O$
$Fe(OH)_3$	+	3HCl	=	$FeCl_3$	+	$3H_2O$ etc.

There are some other compounds like PH_3, NH_3, $C_6H_5NH_2$ (aniline) which are also regarded as bases, though they are not metallic oxides or hydroxides. These compounds form salts with acids but no water is formed.

$$NH_3 + HCl = NH_4Cl$$

Alkalis :—

An oxide of a metal, if soluble in water produces a hydroxide. $Na_2O + H_2O = 2NaOH$; $CaO + H_2O = Ca(OH)_2$ etc.

The term *alkali* is applied to bases that are soluble in water, *soluble basic hydroxides are*, therefore, *alkalis.*

NaOH, KOH, $Ca(OH)_2$, are examples of commonly used alkalis. Aqueous solution of NH_3 is an alkali because it dissolves in water producing ammonium hydroxide : $NH_3 + H_2O = NH_4OH$.

Insoluble hydroxides, e. g. $Al(OH)_3$, $Fe(OH)_3$ etc. are, however, not alkalis, but they are bases and consequently *all bases are not alkalis, but all alkalis are bases.*

The alkalis possess the following characteristic properties :

(1) All alkalis in solution undergo dissociation producing OH^- ions ; $NaOH \rightleftharpoons Na^+ + OH^-$; $NH_4OH \rightleftharpoons NH_4^+ + OH^-$, etc.

(ii) All alkalis spontaneously react with acids producing salt and water ;

$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2H_2O.$$

(iii) All alkalis usually turn the colour of red litmus blue and their solutions give a soapy feel when touched with fingers.

13·4. Basic oxides and hydroxides :

Metallic oxides are called basic oxides, since they exhibit basic properties in reacting with acids to form salts and water. There are, however, some metallic oxides, such as, ZnO, Al_2O_3 etc. which are amphoteric in character, i.e. they react with both the acids as well as bases.

$$ZnO + 2HCl = ZnCl_2 + H_2O$$
$$ZnO + 2NaOH = Na_2ZnO_2 + H_2O$$

Hydroxides may be looked upon as compounds where one or more hydroxyl groups are linked to a metal atom or equivalent electro positive radicals. e.g. KOH, $Cu(OH)_2$, $Fe(OH)_3$ etc.

Metallic hydroxides are bases and if soluble in water, they are termed as alkalis. But $Al(OH)_3$, $Zn(OH)_3$ etc. are amphoteric in character. They react with both the acids as well as alkalis.

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$$
$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O.$$

13·5. **Classification of Bases :**

1. Bases may be classified according to their acidities.

The acidity of a base is its power of neutralising an acid expressed by the number of hydroxyl ions produced through dissociation from one molecule of the base in aqueous solution.

Thus KOH is *mono-acidic base,* because it is dissociated in aqueous solution giving one OH^- ion per molecule. i.e,

$KOH \rightleftharpoons K^+ + OH^-$. Similarly $Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH^-$ is a·diacidic base and so on.

In case of insoluble bases (like CuO, $Pb(OH)_2$, $Fe(OH)_3$ etc), the acidity is usually determined by the number of molecules of monobasic acid (or H^+ ions) with which one molecule of the base reacts completely to form salt and water.

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O$$
$$Fe(OH)_3 + 3HCl = FeCl_3 + 3H_2O$$

Hence CuO is a diacidic base, while $Fe(OH)_3$ is a triacidic base.

2. Depending upon their strengths, the bases can be classified as strong and weak bases. As a base produces OH^- ions in aqueous solution, the concentration of OH^- ions is taken as a measure of the strength of a base. These bases (alkalis), which in aqueous solution undergo practically complete dissociation producing high concentration of OH^- ions are called *strong bases* (*alkalis*), such as NaOH, KOH, $Ca(OH)_2$ etc and those with a

small degree of dissociation are called *weak bases* (*alkalis*). e. g. ammonium hydroxide (NH_4OH).

N.B. For detailed classification of oxides see chapter XVII.

13·6. **Salts** :—Salts are a class of compounds formed by the displacement of the replaceable hydrogen atom (or atoms) of the acid partially or completely, by metals or metal like radicals.

acid	salt	acid	salt
$HCl \rightarrow$	$NaCl$, NH_4Cl	$CH_3COOH \rightarrow$	$(CH_3COO)_2Ca$
$HNO_3 \rightarrow$	KNO_3, $Cu(NO_3)_2$	$HCN \rightarrow$	KCN
$H_2SO_4 \rightarrow$	$NaHSO_4$, K_2SO_4	$H_3PO_4 \rightarrow$	$AlPO_4$, Na_2HPO_4

Such displacement of hydrogen is usually effected by neutralising the acid with an alkali, when salts are formed along with water.

$$\begin{array}{lllllllll} HCl & + & NaOH & = & NaCl & + & H_2O \\ H_2SO_4 & + & 2KOH & = & K_2SO_4 & + & 2H_2O \\ \text{acid} & & \text{base} & & \text{salt} & & \text{water} \end{array}$$

Salts are generally strong electrolytes and remain mostly completely dissociated into ions in solution. On dissociation they give rise to cations other than H^+ ions mentioned as basic radicals and anions other than OH^- ions called acidic radicals. A salt therefore, consists of a metallic (or a basic) radical linked to a non-metallic (or an acidic) radical by ionic bonds.

$KCl \rightleftharpoons K^+ + Cl$; $CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$

$CH_3COONa \rightleftharpoons Na^+ + CH_3COO^-$; $Zn(NO_3)_2 \rightleftharpoons Zn^{++} + 2NO_3^-$

Nomenclature of salts :—In naming salts of *hydracids*, the prefix *hydro*—is dropped and the suffix—*ic* is changed to—*—ide*. Thus,

Acid	salt
HCl (Hydrochloric acid)	NaCl (Sodium chloride)
HBr (Hydrobromic acid)	$ZnBr_2$ (Zinc Bromide)
HCN (Hydrocyanic acid)	KCN (Potassium cyanide).

In naming salts of *oxyacids*, the termination—*ite* is affixed to the name of the salt of any—*ous* acid, and —*ate* to the salt of any —*ic* acid. In other words, the —*ous* acids will produce —*ite* salts and —*ic* acids will give —*ate* salts. Thus,

Acid	Salt
H_2SO_4 (Sulphuric acid)	Na_2SO_4 (Sodium sulphate)
H_2SO_3 (Sulphurous acid)	$CaSO_3$ (Calcium sulphite)
HNO_3 (Nitric acid)	KNO_3 (Potassium nitrate)
HNO_2 (Nitrous acid)	NH_4NO_2 (Ammonium nitrite)
HOCl (Hypochlorous acid)	NaOCl (Sodium hypochlorite)
$HClO_4$ (Per chloric acid)	$NaClO_4$ (Sodium perchlorate)

To name an acid salt, the word *bi* or *hydrogen* is placed between the metallic and the acid parts while a basic salt is indicated by adding the the word *basic* before the name of the salt, Thus,

Acid	Salt
H_2SO_4	$NaHSO_4$ (Sodium bisulphate or Sodium hydrogen sulphate)
H_2CO_3	$CuCO_3$, $Cu(OH)_2$ [basic copper carbonate]

Salts may contain metals which exhibit variable valency. In such cases, when the metal shows the lower valency, the metallic part of the name ends in *–ous*, and when it shows higher valency, it takes the affix *–ic*, Thus

$FeCl_2$(Ferrous chloride), $FeCl_3$(Feric chloride).

13.7. Classification of salts :

The salts have been broadly classified into five categoris :

Normal salts : When all the replaceable hydrogen atoms present in the molecule of an acid are displaced by metal atoms or radicals, normal salts are produced. These salts are generally *neutral* in thir reactions in aqueous solutions, except those fomed by the combination of a strong acid and a weak base or vice-versa

Examples :

acid	no. of replaceable hydrogen atom	normal salts
HCl	1	NaCl, $CaCl_2$, NH_4Cl, etc.
H_2SO_4	2	$ZnSO_4$, Na_2SO_4, $(NH_4)_2SO_4$ etc.
H_3PO_4	3	Na_3PO_4, $Ca_3(PO_4)_2$ etc.

Acid—salts or bi-salts :—These salts are produced by the partial displacement of the replaceable hydrogen atoms of the molecules of a polybasic acid by metal atoms or radicals.

Examples :

Poly basic acid	no. of replacable hydrogen atoms	acid-salts
H_2SO_4	2	$NaHSO_4$, $(NH_4)HSO_4$, $Ca(HSO_4)_2$ etc.
H_3CO_3	2	$NaHCO_3$, $Ca(HCO_3)_2$ etc.
H_3PO_4	3	a) KH_2PO_4, $Ca(H_2PO_4)_2$ etc. b) Na_2HPO_4, $(NH_4)_2HPO_4$, $CaHPO_4$ etc.

All acid salts react with alkalis producing normal salts.

$$\underset{\text{acid salt}}{NaHSO_4} + NaOH = \underset{\text{normal salt}}{Na_2SO_4} + H_2O$$

$$\underset{\text{acid salt}}{KHCO_3} + KOH = \underset{\text{normal salt}}{K_2CO_3} + H_2O$$

Soluble acid salts like $NaHSO_4$, $KHSO_4$ generally give acid reaction to litmus as the anion of an acid salt further ionises in solution producing H^+ ions.

$$NaHSO_4 \rightleftharpoons Na^+ + HSO^-_4 \ ; \ HSO_4^- \rightleftharpoons H^+ + SO_4^{--}$$

But $NaHCO_3$ is slightly alkaline in its reaction as the bicarbonate ion tends to accept proton in aqueous solution.

$$NaHCO_3 \rightleftharpoons Na^+ + HCO^-_3 ; \ HCO^-_3 + H^+ \rightleftharpoons H_2CO_3$$

Basic Salts :—These salts are produced when the hydroxyl groups present in a molecule of poly acidic base are only partially replaced by acid redicals or anions of an acid. Such salts are generally formed by the reaction of an acid with a proportion of the base higher than that required to form a normal salt. These salts are generally basic in character and react with excess acid to form normal salts.

Examples :—

$Pb\,(OH)_2 + HCl = Pb\,(OH)\,Cl + H_2O$

$2Cu\,(OH)_2 + H_2CO_3 = Cu(OH)_2, CuCO_3 + 2H_2O$

$Bi\,(OH)_3 + HNO_3 = Bi\,(OH)_2NO_3 + H_2O$ etc.

(iv) *Double Salts* :—When solutions of two normal salts are mixed in correct proportions and allowed to crystallise, the solid crystals are found to contain both the salts with some water of crystallisation. These are called double salts. Such salt exists only in the solid state and breaks up in solution into its constituent normal salts, which on dissociation give all the ions contained in the simple salts. A double salt conforms to the law of constant proportions, Examples of double salts are, Alums, e.g., potash alum – K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$, Mohr Salt —Ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4$, $6H_2O$ etc. Potash alums formed by the crystallisation of the solution containing K_2SO_4 and $Al_2(SO_4)_3$ in molecular proportions, gives all the ions of its constituent salts when dissolved in water, thus—

$$K_2SO_4, Al_2(SO_4)_3, 24H_2O \rightleftharpoons 2K^+ + 2Al^{+++} + 4SO_4^{--} + 24H_2O$$

(v) *Complex Salts* :—A complex salt is a salt which contains one or more complex ions formed by the co-ordination of a number of negative ions or neutral molecule (called ligands) to a central metal ion. Complex salts are usually prepared by mixing of two simple salts. The salt thus formed is a distinct chemical substance in the solid state as well as in solution. In aqueous solution, it does not dissociate into all the simple ions of the salts from which it is obtained, but yields complex ions along with the simple ions. Let us take an example,—Potassium Ferrocyanide, $K_4Fe(CN)_6$, is a complex salt and is obtained by adding excess of potassium cyanide to a solution of ferrous sulphate, until the precipitate of ferrous cyanide redissolves.

$FeSO_4 + 2KCN = Fe(CN)_2 + K_2SO_4$;

$$Fe(CN)_2 + 4KCN = K_4[Fe(CN)_6].$$

From its composition, it appears to be a mixture offerrous cyanide and potassium cyanide in the proportion of one to four. But its solution does not respond to the test of either ferrous ion or those of the cyanide ion ; because the salt never dissociates into K^+, Fe^{+2} and CN^- ions. On the other hand, it ionises in solution as $K_4Fe(CN)_6 \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$, the whole of Fe^{++} ion is practically transfomed into complex ferro—cyanide, $[Fe(CN)_6]^{4-}$ ion, which remains in tact in solution and has its distinctive reaction.

Other examples of such salts are :

a) Cuprammonium sulphate $[Cu(NH_3)_4]SO_4$, which ionises as $[Cu(NH_3)_4]SO_4 \rightleftharpoons [Cu(NH_3)_4]^{++} + SO_4^{--}$

b) Hexaammino cobaltic chloride $[CO(NH_3)_6]Cl_3$, ionises as

$$[CO(NH_3)_6]Cl_3 \rightleftharpoons [CO(NH_3)_6]^{+++} + 3Cl^-$$

c) Potassium ferricyanide $K_3Fe(CN)_6$, which ionises as

$$K_3Fe(CN)_6 \rightleftharpoons 3K^+ + [Fe(CN)_6]^{3-}$$

Some complex ions may, however, partly dissociates in solution, for example, Argento ammonium chloride $[Ag(NH_3)_2]Cl$ dissocitates in aqueous solution as follows .—

$[Ag(NH_3)_2]Cl \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$; $[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$. the concentration of simple Ag^+ is however, so small that it is negligible.

13·8. Methods of Preparation of acids, bases and salts :—

(A) **Acids** :—There are a number of ways for preparing acids.

(i) Some hydracids may be prepared by direct union of hydrogen with non-metal :

$$H_2 + Cl_2 = 2HCl \; ; \qquad H_2 + S = H_2S$$

(ii) acidic oxides when soluble in water give acids :

$$SO_3 + H_2O = H_2SO_4 \; ; \qquad N_2O_5 + H_2O = 2HNO_3$$

(iii) The decomposition of non-metallic chlorides by water, called hydrolys is, also produces acids. CCl_4 is, however. stable towards water :

$PCl_3 + 3H_2O = 3HCl + H_3PO_3$ (Phosphorus acid)

$SiCl_4 + 4H_2O = 4HCl + H_4SiO_4$ (ortho-silicic acid)

(iv) Less volatile but strong acid, such as sulphuric acid, reacts with the salt of a more volatile acid to give off the acid.

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$
$$FeS + H_2SO_4 = FeSO_4 + H_2S$$

(v) Hot and concentrated nitric acid oxidises directly some non-metals to their oxy acids :

$$S + 2HNO_3 = H_2SO_4 + 2NO$$
$$4P + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2$$
$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O$$

Bases : (i) Since bases are metallic oxides, they may be prepared by direct oxidation of the metals :

$$2Cu + O_2 = 2CuO \; ; \qquad 2Mg + O_2 = 2MgO.$$

(ii) The oxides are also obtained by heating some carbonates, hydroxides or nitrates of the metals.

$$CaCO_3 = CaO + CO_2 \; ; \quad 2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$
$$Cu(OH)_2 = CuO + H_2O$$

(iii) The insoluble hydroxides of metals are prepared by precipitating the same from aqueous solution of salts of the metals by alkali.

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4$$
$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl$$

(iv) The soluble metallic hydroxides or alkalis are prepared by dissolving the soluble oxides or by the action of some metals on water.

$$Na_2O + H_2O = 2NaOH \; ; \quad CaO + H_2O = Ca(OH)_2$$
$$2K + 2H_2O = 2KOH + H_2 \; ; \quad Ca + 2H_2O = Ca(OH)_2 + H_2$$

Salts :—Salts are prepared by various methods :—

(i) By the action of an acid directly on a metal ;

$$Mg + 2HCl = MgCl_2 + H_2 \; ; \quad Zn + H_2SO_4 = ZnSO_4 + H_2$$

(ii) By the action of an acid upon a base. The method also includes the reaction between basic and acidic oxides ;

$$Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O \; ;$$
$$HCl + NaOH = NaCl + H_2O$$
$$CaO + CO_2 = CaCO_3$$

(iii) By the action of less volatile acid on the salt of more volatile acid. An insoluble salt may also be prepared by this method :

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3 \; ; \quad BaCl_2 + H_2SO_4 = 2HCl + BaSO_4$$

(iv) By double decomposition between solutions of two salts, an insoluble salt may be produced ;

$$AgNO_3 + NaCl = AgCl \downarrow + NaNO_3$$
$$BaCl_2 + Na_2SO_4 = BaSO_4 \downarrow + 2NaCl$$

(v) By direct combination of a metal and a non-metal ;

$$2Fe + 3Cl_2 = 2FeCl_3 \; ; \quad Hg + S = HgS.$$

(vi) By displacement of the metal of a salt in solution by another more electropositive metal ;

$$Fe + CuSO_4 = FeSO_4 + Cu \; ; \quad Zn + 2AgNO_3 = Zn(NO_3)_2 + 2Ag.$$

13·9. New ideas about acids and bases : Definitions based on proton transference.

Lowry and Bronsted have proposed somewhat different definitions for acid and base.

We know that a hydrogen atom consists of only one proton in its nucleus and just one electron outside the nucleus. When it loses this single electron, H^+ ion is formed, which is therefore nothing but a bare 'proton'. The proton of the H^+ ion in water remains attached to a molecule of water forming H_3O^+, called hydronium ion, $H^+ + H_2O \rightleftharpoons H_3O^+$.

Lowry and Bronsted pointed out that the reaction that occurs when an acid dissolves in water to yield hydronium ions is essentially a transference of a proton (H^+) from a molecule of the acid to a water molecule. On the basis of this, Lowry and

Bronsted, in 1923, advanced the protonic concept for acids and bases. The concept is ;

"An acid is any molecule, radical, or ion, which has a tendency to give up protons i.e., acts as a proton donor ; and a base is a substance (molecule, radical or ion) which has the tendency to take up protons i.e., acts as a proton acceptor."

Thus, HCl, CH_3COOH, HNO_3, HSO_4^- ion etc. are all acids as they readily give protons in aqueous media ;

$$HCl \rightleftharpoons H^+ + Cl^- \ ; \quad CH_3COOH \rightleftharpoons H^+ + CH_3COO^- \ ;$$
$$HNO_3 \rightleftharpoons H^+ + NO_3^- \ ; \quad HSO_4^- \rightleftharpoons H^+ + SO_4^{--}.$$

On the other hand. NH_3, OH^-, CO_3^{--}, SO_4^{--} ions etc.. are bases as these would easily accept protons and be converted into acids.

base acid

$$NH_3 + H^+ \rightleftharpoons NH_4$$
$$OH^- + H^+ \rightleftharpoons H_2O$$
$$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$$

base acid

$$CO_3^{--} + H^+ \rightleftharpoons HCO_3^-$$
$$SO_4^{--} + H^+ \rightleftharpoons HSO_4^-$$
$$Cl^- + H^+ \rightleftharpoons HCl$$

One of the significant results of this concept is that a neutral molecule as well as an ion can possess acidic or basic character in solution.

Water has a special quality. Water is a very weak electrolyte which ionises as follows :—

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$H^+ + H_2O \rightleftharpoons H_3O^-$$

$$\text{or,}\quad H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

This shows that water can be either an acid or a base ; a proton released by one molecule is accepted by the other.

13·10. Hydrolysis of Salts :—

Normal salts are formed by the complete neutralisation of an acid by an alkali. In every neutralisation, $H^{\pm}$ ions of the acid unite with OH^- ions of the alkali to produce practically unionised molecules of water. Water is neutral, its minute dissociation ($H_2O \rightleftharpoons H^+ + OH^-$) gives equal amounts of H^+ ions of OH^- ions.

It will be seen later that in any aqueous solution, the product of the concentrations of H^+ and OH^- ions. i.e. $C_{H^+} \times C_{OH^-}$ is always constant. If the amount of H^+ ion is greater than OH^- ions, the solution is acidic, if it is less, the solution is alkaline. But if they are equal, the solution will be neutral. It is expected that solutions of normal salts should be neutral, since there are no replaceable H^+ or OH^- ions in these salts. This is indeed true in many cases like the solutions of NaCl, KNO_3, $CaCl_2$, Na_2SO_4 etc. i.e. in the case of salts derived from strong acids and strong bases. Such salts simply ionise in solution ;

$$NaCl \rightleftharpoons Na^+ + Cl^- \; ; \; KNO_3 \rightleftharpoons K^+ + NO_3^- \; ;$$
$$Na_2SO_4^{--} \rightleftharpoons 2Na^+ + SO_4^{--}.$$

But the solution of many other salts like those of Na_2CO_3, NH_4Cl, KCN, $FeCl_3$, CH_3COONa etc. are found to be either acidic or alkaline. It is known that salts derived from weak acids or weak bases or from both behave in this way.

In solution, the salts of weak acids or weak bases are reversibly split up by water to produce the original free acid and the free base from which the salt was produced. The solution will behave acidic or alkaline depending upon whether the liberated acid is stronger than the liberated base or not. This process of splitting up of a salt by water is called *hydrolysis* of salts. The process may be considered as the reverse of neutralisation.

Neutralisation : $HCl + NH_4OH = NH_4Cl + H_2O$

Hydrolysis : $NH_4Cl + H_2O = NH_4OH + HCl.$

The resulting salt solution reacts acidic or alkaline according as the acid or base, formed due to hydrolysis, is relatively strong.

Obviously, three different cases of salt hydrolysis may occur, that is, hydrolysis of salts derived from—

(i) Weak acids and strong bases,

(ii) Strong acids and weak bases,

(iii) Weak acids and weak bases,

The salts produced from strong acids aud strong bases do not undergo hydrolysis.

In the light of Arrhenius theory of electrolytic dissociation, it may be considered that strong electrolytes, i.e. all salts, strong acids and strong bases dissociate practically completely in solution, where as the weak electrolytes like weak acids and weak bases, are only slightiy dissociated in solution. On this basis let us discuss the three cases of hydrolysis of salts :

(i) Hydrolysis of salts of weak acid and strong bases give rise to an alkaline solution. For example, when sodium acetate (salt formed from weak acid, CH_3COOH and strong base, N_aOH) is dissolved in water, it undergoes hydrolysis producing strong base, NaOH and weak acid, CH_3COOH.

$$CH_3COONa + H_2O \rightleftharpoons \underset{\text{Strong}}{NaOH} + \underset{\text{Weak}}{CH_3COOH}$$

or, $CH_3COO^- + Na^+ + H_2O \rightleftharpoons Na^+ + OH^- + CH_3COOH.$

In the resulting solution, NaOH being strong produces large amounts of OH^- ions but CH_3COOH being weak liberates very little H^+ ions, hence the solution will be alkaline due to excess of OH^- ions.

All salts produced from weak acids and strong bases react alkaline in aqueous solution, viz ; KCN, Na_2CO_3 etc.

(ii) Hydrolysis of salts of strong acids and weak bases gives rise to an acidic solution. For example, when ammonium chloride (salt formed from strong acid, HCl and weak base, NH_4OH) is dissolved in water, it undergoes hydrolysis yielding the strong acid, HCl and weak base, NH_4OH.

$$NH_4Cl + H_2O \rightleftharpoons \underset{\text{strong}}{HCl} + \underset{\text{weak}}{NH_4OH}$$

or, $NH_4^+ + Cl^- + H_2O \rightleftharpoons H^+ + Cl^- + NH_4OH.$

In the resulting solution, weak base NH_4OH scarcely dissociates, but the strong acid, HCl, practically completely dissociates to produce large amount of H^+ ions. As a result, there is an excess ofH $^+$ ions to render the solution acidic. Thus the solutions of salts produced from strong acids and weak bases are always acidic ; for example, $FeCl_3$, $CuSO_4$, $(NH_4)_2SO_4$, etc.

(iii) Hydrolysis of salts of weak acids and weak bases :—

A salt of this type undergoes rapid hydrolysis producing the weak acid and the weak base from which the salt was obtained. The resulting solution may be acidic, alkaline or even neutral depending upon the relative degrees of dissociation of the weak acids and bases formed. For example :

(a) $HCOONH_4 + H_2O \rightleftharpoons HCOOH + NH_4OH$

Ammonium formate weak weak

Since formic acid, HCOOH, though weak dissociates to a greater extent than NH_4OH, hence the solution is sightly acidic.

(b) $(NH_4)_2CO_3 + 2H_2O \rightleftharpoons 2NH_4OH + H_2CO_3$

weak weak

Here, the dissociation of NH_4OH is somewhat larger than that of carbonic acid, H_2CO_3, hence the solution is sightly alkaline.

(c) $CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

weak weak

In the resulting solution both the acid and the base, are equally weak and dissociate slighly and almost in equal degree. Hence this solution is practically neutral.

13·11. Equivalent weights of acids, bases and salts.

(i) *Equivalent weight of acids :—The equivalent weight of an acid is the number of parts by weight of the acid which contains 1·008 parts by weight of replaceable hydrogen, i.e., one atom of replaceable hydrogen.*

The number of replaceable hydrogen atoms in the molecules of an acid is called its basicity. Hence,

$$\text{Equivalent weight of an acid} = \frac{\text{molecular wt. of the acid}}{\text{basicity}}.$$

The gm-equivalent of the acid is its equivalent weight expressed in grams. Thus,

$$\text{Gram equivalent weight of an acid} = \frac{\text{Gram-molecular weight (mole) of the acid}}{\text{basicity}}$$

i.e., a gram equivalent of an acid is that weight of it in grams which contains 1·008 gram of replaceable hydrogen.

Examples :

Acid	Mol. wt.	Basicity	Eq. wt.	gram-equv.
	(M)	(b)	(M/b)	
Hydrochloric, HCl	36·5	1	36·5	36·5 gms
Nitric, HNO_3	63·0	1	63·0	63·0 gms
Acetic, CH_cCOOH	60·0	1	60·0	60·0 gms
Sulphuric, H_2SO_4	98·0	2	49·0	49·0 gms
Oxalic, $(COOH)_2, 2H_2O$	126·0	2	63·0	63·0 gms
Phosphoric, H_3PO_4	98·0	3	32·67	32·67 gms

Equivalent weight of an acid may also be defined as that part by weight of the acid which neutralises one equivalent of a base. Thus, in the reaction.

$$\underset{36\cdot5}{HCl} + \underset{40}{NaOH} = NaCl + H_2O$$

36·5 parts by weight of HCl neutralise 40 parts by wt. of NaOH. It will be seen later that 40 is the equivalent weight of the alkali NaOH. Hence equivalent weight of HCl is 36·5.

(ii) *Equivalent weight of bases* : *The equivalent weight of a base is the number of parts by weight of the base which neutralises one equivalent weight of an acid ; or the parts by weight of the base which contains a replaceable OH group* (*i.e., 17 parts by weight of the replaceable OH group*).

The number of OH groups present in a molecule of the base is its acidity. Hence,

$$\text{Equivalent wt. of the base} = \frac{\text{Molecular weight of the base}}{\text{acidity}}$$

The gram-equivalent weight of a base is its equivalent weight expressed in grams. Thus,

Gram equivalent weight of a base

$$= \frac{\text{gram molecular wt. of the base}}{\text{acidity.}}$$

Examples :—

$$\underset{74}{Ca(OH)_2} + \underset{98}{H_2SO_4} = CaSO_4 + 2H_2O$$

The equivalent wt. of $H_2SO_4 = 49$. ∴ one gm. equivalent of H_2SO_4 (i.e. 49 gms) is neutralised by 37 gms. of $Ca(OH.)_2$. Therefore, eq. wt. of $Ca(OH) = 37$. *OR,*

$$\text{Eq. wt. of } Ca(OH)_2 = \frac{\text{Mol. wt.}}{\text{acidity}} = \frac{74}{2} = 37.$$

Base (alkali)	Mol. wt. (M)	acidity (*a*)	Eq. wt. (*M*/*a*)	gm.equv.
Caustic Soda, NaOH	40	1	40	40 gms
Caustic potash, KOH	56	1	56	56 gms
Calcium hodroxide, $Ca(OH)_2$	74	2	37	37 gms
Barium hydroxide, $Ba(OH)_2$	171	2	85·5	85·5 gms
Aluminium hydroxide, $Al(OH)_3$	78	3	26	26 gms
Ammonium hydroxide, NH_4OH	35	1	35	35 gms

In case of basic oxide the equivalent weight may be obtained by determining the parts by wt. of the basic oxide which neutralise completely one equivalent of an acid. Thus

$$MgO + 2HCl = MgCl_2 + H_2O$$

20 parts by wt. of MgO neutralise 35·5 parts by weight (i.e. 1 equivalent) of HCl. Therefore equivalent wt. of $MgO = 20$, its gm equivalent = 20 gms.

(iii) *Equivalent weight of Salts:* The equivalent weight of a salt is that part by weight of the salt which contains one equivalent of the metal (or metal like radical) present in it.

Now, one equivalent of the metal is its atomic weight divided by its valency. Hence, equivalent weight of a salt is its molecular weight divided by total valency of the metal atom present in a molecule.

∴ Equivalent wt. of a salt

$$= \frac{\text{Molecular wt. of the salt}}{\text{Total number of valences of the metal atoms}}$$

$$= \frac{\text{Mol. wt. of the salt}}{\text{No. of metal atoms} \times \text{its valency}}$$

A gram equivalent weight of the salt is its equivalent weight expressed in grams.

Examples :

Salt	Mol. wt. (M)	Total valency of metal atoms	Equv. wt.
Sodium Chloride, NaCl	58·5	1×1	58·5
Sodium Carbonate, Na_2CO_3	106·0	2×1	106/2=53
Aluminium Sulphate, $Al_2(SO_4)_3$	342	2×3	342/6=57
Copper Sulphate, $CuSO_4, 5H_2O$	249·5	1×2	249·5/2=124·75

In the case of salts which react with acids, such as carbonate or bi-carbonate, equivalents may be determined with reference to the acids. The equivalent of the salt=its molecular wt. divided by the number of equivalents of an acid with which one mole of the salt react.

$$\underset{106}{Na_2CO_3} + \underset{\text{2 equivalents}}{2HCl} = 2NaCl + CO_2 + H_2O$$

$$\underset{84}{NaHCO_3} + \underset{\text{1 equivalent}}{HCl} = NaCl + H_2O + CO_2$$

∴ 53 gm of Na_2CO_3 and 84 gms of $NaHCO_3$ react individually with 1 equivalent of HCl. Hence Eq. wt. of Na_2CO_3 and $NaHCO_3$ one 53 are 84 respectively.

The equivalent weight of a compound, in general, is that part by weight of the compound which reacts with one equivalent of an element or a compound of known equivalent weight. The equivalent wt. of a substance will depend upon the particular reaction in which it takes part.

Exercise—13

1. Define and illustrate the following terms—
   (a) acid, (b) base, (c) salt.
   What are their characteristic properties ?

2. In what different ways the acids. bases and also the salts are classified ? Has the reaction of a salt anything to do with the classification ?

3. (a) Both alcohol and caustic soda molecules have OH groups, then why alcohol is not considered as an alkali ?

(b) Justify the following statements—

(i) All acids are hydrogen compounds but all hydrogen compounds are not acids.

(ii) All alkalis are bases but all bases are not alkalis.

(iii) Upon adding sodium carbonate to an aqueous solution of ferric chloride, ferric carbonate is not precipitated.

4. What is meant by salt hydrolysis ? What types of salts usually undergo hydrolysis ? State with reasonings. Which of the salts in solution would give acidic, alkaline or neutral reaction ?

(a) sodium acetate ; (b) ferric chloride ; (c) ammonium acctate ; (d) aluminium sulphate, (e) sodium chloride.

5. Write explanatory notes on—

(a) acid salts and basic salts
(b) double salt and complex salt
(c) basicity of an acid and acidity of a base
(d) neutralisation and hydrolysis

6. Give the acidity and basicity of the following—

(i) CaO (ii) H_3PO_4, (iii) $Ba(OH)_2$, (iv) $H_2S_2O_3$, (v) HPO_3 (vi) MnO_2, (vii) $Al(OH)_3$ (viii) NH_3,

7. Which of the following is the correct answer ?

In a neutral solution,

(i) there are no H^+ ions, (ii) There are no OH^- ions,

(iii) There are neither H^+ nor OH^- ions.

(vi) H^+ and OH^- are present in very small but equal in number.

8. How do you explain the following—

(i) solution of K_2CO_3 turns red litmus blue but a solution of copper sulphate turns blue litmus red.

(ii) A solution of $(NH_4)_2SO_4$ is acidic but a solution of CH_3COONH_4 is neutral.

(iii) A solution of ferric chloride, on standing, gives a precipitate of ferric hydroxide.

9. What do you mean by the strength of an acid or of a base ? How do you explain that "some acids are strong and some are weak". Give names and formulas of 3 strong and 3 weak acids as well as bases.

10. (a) How do you define the equivalent weights of (i) acids, (ii) bases and (iii) salts. Give exampies.

(b) Calculate the eqivalent weight of the following substances—

(i) $NaHCO_3$, (ii) $CaCO_3$, (iii) $Fe_2(SO_4)_3$, (iv) CH_3COOH, (v) $Zn(NO_3)_2$, (vi) $C_6H_4(COOH)_2$, (vii) HCN.

CHAPTER—XIV

ACIDIMETRY AND ALKALIMETRY

In order to ascertain quantitatively the composition of a given substance, two methods of analysis are generally employed : (i) gravimetric method and (ii) volumetric method. In *gravimetric analysis*, the composition of the substance is determind by direct weighing the constituents in some weighable form in a chemical balance. This is a tedidus and time consuming process. In *volumetric analysis*, the quantity of a substance present in a given sample is determined not by direct weighing, but by finding out the volume of the solution of the given sample required to just completely react with a definite volume of solution of another substance. It is often advantageous to follow this process. To measure the volumes of solutions correctly, some common apparatus like burette, pipette, volumetric flask, measuring cylinder etc., correctly calibrated are used. Acidimetry and alkalimetry are the volumetric methods of analysis with the help of which the strength of an acid and alkali solutions are determined.

14·1. **Neutralisation ;**

In neutralisation reactions, the acids react with bases in equivalent amounts to form salt and water. The resulting solution usually becomes neutral as it contains neither an excess of the acid nor of the base. The H^+ ions of the acid and the OH^- ions of the base (alkali) are united producing undissociated water molecules. That is,—

$$HCl + NaOH = NaCl + H_2O$$

or, $$H^+ + Cl^+ + Na^+ + OH = Na^+ + Cl^- + H_2O.$$

14·2 **Indicators :**

Indicators are some organic substances which indicate by change of colour whether a solution is acidic, alkaline or neutral.

Any indicator takes one colour in acidic medium and a different colour in alkaline medium. Litmus is an indicator which turms red in acids and blue in alkalis. So, to test the nature of a solution, a few drops of litmus solution is added to it, if the colour turns red the solution is acidic and if it turns blue the solution is alkaline. An indicator which shows a sharp contrast of colour in solutions just acidic or just alkaline is a good indicator. A list of indicators with their colours shown in acidic, alkaline and neutral media is given below.

Indicators	colour in acidic soln.	colour in alkaline soln.	colour in neutral soln.
1. Litmus	red	blue	purple or violet
2. methyl orange	red or pink	yellow	orange
3. phenolphthalein	colourless	pink	colourless
4. methyl red	red	yellow	orange

These indicators are often called "acid-base" or "neutralisation" indicators as they indicate the acidic or alkaline nature of a solution. These are also used in volumetric analysis to indicate, by change of colour, the termination (i.e., end point) of neutralisation reactions between acids and bases. There are other kinds of indicators which by their colour changes show if a subtance in solution is in the oxidised or reduced state and as such are used to indicate the termination of oxidation reduction reactions ; these are called redox indicators.

14·3. Titration :

Titration is an operation or technique in which the volume of the solution of a given substance required to just completely react with a definite volume of solution of another substance is found out in presence of an appropriate indicator. Such determinations lead to the estimation of the concentration of one solution if that of the other is known. In practice, the acid base titration is done in the following way to carry out neutralisation reaction.

Usually a known volume of an alkali solution (say 25 c.c. of NaOH) is taken in a beaker or conical flask by means of a pipette and a few drops of phenolphthalein indicator is added to it and it turns pink. The acid (say H_2SO_4) solution is taken in a burette, which is clamped in a vertical position. The acid is then added drop by drop to the alkali solution with stirring so that the alkali is gradually neutralised, When the volume of the acid solution added is just sufficient to neutralise the alkali taken, the pink colour suddenly disappears and the mixture is colourless. This point exactly where the colour change of the indicator occurs is called the equivalence point or end point of titration. The volume of acid added is noted from the burette,

Let the burette reading at the equivalence point be 15 c,c. Then 25 c.e. of the NaOH solution = 15 c,c. of the H_2SO_4 solution. Now we know from the reaction,

$$\underset{2\times 40}{2NaOH} + \underset{98}{H_2SO_4} = Na_2SO_4 + 2H_2O$$

80 gm of NaOH neutralises 98 gm H_2SO_4. So, if the amount of NaOH in the 25 c.c. solution taken for the experiment is known the amount of H_2SO_4 present in 15 c.c. of the acid solution can be ascertained.

The method of determining the strength of an acid solution by titrating it with a solution of alkali of known strength is called *acidimetry*. And the method of determining the strength of an alkali solution by titrating it with an acid solution of known strength is called alkalimetry.

N.B. The defiinition of acidimetry and alkalimetry, according some authors are just the reverse of what are stated here.

14·4. Suitability of indicators :

Indicators are used to indicate the end point of titrations, i.e., to determine the point when equivalent amounts of acids and bases react to produce salt and water, the solution does not contain any excess acid or alkali. As already stated, the indicators have various colours (and in some cases are colourless) in acid solution and have quite different colours in alkaline solution. So by the production of an intermediate colour in proceeding from acidity to alkalinity, or vice versa, the indicators will indicate when exactly the equivalence point is reached. The selection of a suitable indicator for this purpose is of primary importance.

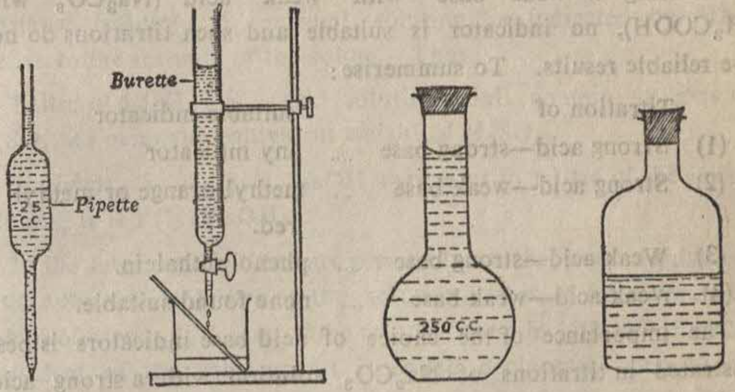


Fig. 14-1. The operation of titration

The change of colour with different indicator does not take place exactly at the equivalence-point or the theoretical neutral point. Some indicators, like *methyl orange*, *methyl red* change their colour when the solution is still faintly acidic. On the other hand, the indicator *phenolphthalein* shows a colour change when the solution is faintly alkaline. This colour change actually depends upon the hydrogen ion concentration of the solution.

In titrating a weak base (NH_4OH, Na_2CO_3 etc.) with a strong acid (HCl, H_2SO_4, etc.). when the equivalence point is reached the solution will contain a salt of weak base-strong acid. Such a solution will be slightly acidic due to hydrolysis. Hence an indicator which shows change of colour (i.e. end-point) in slightly acidic medium should be used. Methyl orange or methyl red are such indicators. Similarly in titrating a strong base (NaOH etc.) with a weak acid (CH_3COOH) when equivalence point is reached, the solution will contain a salt of weak acid-strong base and hence will be slightly alkaline due to hydrolysis. In such a titration, therefore, phenolphthalein indicator should be used, as it shows a colour change in faintly alkaline medium. For titrating strong acids with strong bases, any indicator is suitable because at the equivalence point the solution will contain a salt of strong acid-strong base, which does not undergo hydrolysis and hence the solution at the end point is exactly neutral. Lastly, in titrating a weak base with weak acid (Na_2CO_3 with CH_3COOH), no indicator is suitable and such titrations do not give reliable results. To summerise:

	Titration of	suitable indicator
(1)	Strong acid—strong base	any indicator
(2)	Strong acid—weak base ...	methyl orange or methyl red.
(3)	Weak acid—strong base	phenolphthalein.
(4)	Weak acid—weak base	none found suitable.

The importance of the choice of acid base indicators is best illustrated in titrations of Na_2CO_3 solution with a strong acid (HCl) solution. If phenolphthalein indicator is used to detect the end point, its pink colour disappears when only half of Na_2CO_3 is neutralised. This is because of the fact that the reaction at first proceeds as $Na_2CO_3 + HCl = NaHCO_3 + NaCl$.

So long as Na_2CO_3 is present, phenolphthalein shows pink colour, but when the former transformed completely into $NaHCO_3$, phenolphthalein is incapable of registering the alkaline colour. In other words, $NaHCO_3$ solution is not alkaline to phenolphthalein. So, with phenolphthalein indicator only half of neutralisation can be carried out.

On the other hand, if methyl orange indicator be used, the $NaHCO_3$ solution would also be shown as alkaline and the end-point of the reaction will now be indicated when the whole of Na_2CO_3 is neutralised.

14·5. Strength of solution :

The strength or concentration of a solution refers to the amount of solute present in a given volume of the solution. The concentration may be expressed in different units, such as, gms of solute per litre of the solution, gm. moles/litre of the solution, normality, molarity (formality) or molality. Occasionally, strength is also given on percentage basis.

Normality : Normal solutions—A normal solution is such a solution, one litre of which contains one gram equivalent of the substance (solute). A normal solution is indicated by "IN" prefixd to the formula of the solute. Thus,

1 litre of 1 (N) H_2SO_4 acid solution shall contain 49 gms of H_2SO_4, 49 being the equivalent weight of H_2SO_4.

Similarly, if 40 gms NaOH is present in 1 litre of the alkali solution, it is 1 (N) NaOH.

In the same way, if there are present twice the gram equivalent of the substance in 1 litre of the solution, it is twice normal or 2 (N) solution. If 1 litre of the solution contain 1/10 th. of gram-equivalent of the substance it is called decinormal or $N/10$ or 0·1 (N) solution, and so on. Hence the number of gram equivalents of solute dissolved in 1000 c.c. of a solution is called the normality of the solution.

Suppose, W gm of substance is present in V litres of the solution and suppose E is the equivalent weight of the substance.

Then the solute present in V litres $= W$ gms $= \frac{W}{E}$ gm. equiv.

$\therefore$ the solute present in 1 litre $= \frac{W}{E \times V}$ gm. equivalent.

Hence, the normality of the solution $(N) = \frac{W}{V \times E}$

$$\therefore \quad \text{Normality } (N) = \frac{\text{wt. of solute in gm. per litre}}{\text{gram-equivalent}}$$

or, wt. of solute in gm. per litre = normality × gm. equivalent.

Example :—1f 4 litres of a solution contain 10.6 gm Na_2CO_3 its nomality will be calculated as :

The amount of Na_2CO_3 per litre $= 10{\cdot}6 \div 4 = 2{\cdot}65$ gm.

The equivalent wt. of $Na_2CO_3 = \frac{106}{2} = 53$.

$\therefore$ Normality of the solution $= \frac{2{\cdot}65}{53} = {\cdot}05$ (N)

Molarity : A molar solution of a substance contains one mole (i.e., one gram molecular wight) of it per litre of the solution. The strength is indicated by prefixing '1 M' before the formula of the solute. Thus,

One molar H_2SO_4 or 1 (M) H_2SO_4 acid solution means 98 gms of H_2SO_4 acid is present in one litre of solution. Similarly, 1 molar (1M) glucose solution ($C_6H_{12}O_6$) contains 1 mole (i.e , 180 gm) of glucose per litre of solution.

The molarity of a solution is defined as the number of moles of the solute present per litre of the solution.

Suppose, w gms of a substance, having molecular weight m, is present in v liter of solution. Then the number of moles of the substance present in v litre of solution $= \frac{w}{m}$.

$$\therefore \text{ the molarity (M) of the solution} = \frac{w}{m \times v}$$

$$= \frac{\text{wt. of the solute per litre}}{\text{mol. wt. of the solute}}$$

$\therefore$ the weight of solute per litre = molarity × molecular weight.

Example :—If 500 c.c. of a solution contains 15 gm. NaOH in solution, its molarity will be $\frac{15 \times 2}{40} = 0{\cdot}75$ (M)

It may be noted that, if the molecular weight and the equivalent weight of a substance are the same, its *normal* solution will be the same as its *molar* solution. Thus for NaOH, both the molecular weight and the equivalent weight are equal to 40, so, its normal and molar solutions are the same. But in case of H_2SO_4 the concentration of molar solution will be twice the concentration of the normal solution as mol. wt. is twice the equivalent weight.

Formality : The salts such as NaCl, KCl, remain as ions in the solid state as well as in solution, To speak of their molecular weight or molar solution is not really correct, as they do not exist as molecules. For the solution of such strong electrolytes, which actually do not exist in the molecular forms, the unit of concentration is formality (F). One formal solution contains 1 gram formula weight i.e. one formula weight in gram of the solute per litre of solution. The symbol of the strength is "$1F$". Hence *formality* (F) is the number of gram formula weight of solute per litre of solution. Thus, if w gm of the substance having formula weight f_w, be present in v litres of the solution, its formality is

$$F=\frac{W/f_w}{v}=\frac{W}{v\times f_w}=\frac{\text{wt. of the substance per litre.}}{\text{formula weight }(f_w)}$$

or, wt. of the substance per litre = formula weight × formality.

If the formula of a solute is the same as its correct molecular formula representing the molecules actually present in the solution, then formality and molarity become identical. Thus, a $1F$ solution of glucose having the molecular formula $C_6H_{12}O_6$, is also a $1M$ solution. But $1F$ solution of Feric chloride is not its $1\ M$ solution, since it is completely dissociated into Fe^{+3} and Cl^- ions and no $FeCl_3$ molecules are actually present in solution, hence it is better stated as $1\ M$ in Fe^{+3} ions and $3M$ in Cl^- ions.

Molality : A molal solution of a substance contains 1 mole of it per 1000 gm. of the solvent. Hence molality (m) is the number of moles of solute per 1000 gram of solvent. Thus,

$$\text{Molality }(m)=\frac{\text{Number of moles of solute}\times 1000}{\text{weight of solvent in grams}}.$$

14.6. The Normality Principle :

Determination of the strength of a solution by titrimetric methods (acidimetry and alkalimetry) is based on some principles which are given below.

(*1*) *Volume of given solution is inversely proportional to its strength, i.e., if the volume is increased, the strength is proportionately decreased and vice versa, for any solution.*

In 1 N strength, 1 gm-equivalent is present in 1000 c.c. of the solution

In N/2 strength, 1 gm-equivalent is present in 2 × 1000 c.c. of the solution.

In N/10 strength, 1 gm-eqivalent is present in 10 × 1000 c.c. of the solution.

Therefore, 1000 cc. of 1 N soultion = 2000 cc. ofN/2 solution.
= 10000 c.c., of N/10 solution.

As the strength (normality) of the solution decreases, the volume containing one gm-equivalent increases, In a more general way,

Let 1 c.c. of a normal (N) solution contains p equivalents of a solute,

then $(x \times y)$ c.c. of the (N) solution contains $(p \times x \times y)$ equivalents of solute.

Also 1 c.c. of y (N) solution contains $(y \times p)$ equivalents of the solute.

then x c.c. of y (N) solution contain $(x \times y \times p)$ equivalents of solute

∴ x c.c. of y (N) solution $= (x \times y)$ c.c. of (N) solution, since both the solutions contain $(p \times x \times y)$ equivalents of solute.

(2) *Acids and bases neutralise each other in equivalent amounts. Hence, solution of acids and bases of the same normality must neutralise in equal volumes.*

We know one litre solution of any 1 N acid or alkali contains 1 gm-equivalent of the solute.

Hence 1 litre of 1 (N) acid solution will be neutralised by 1 litre of 1 (N) alkali solution since each solution contains 1 gm-equivalent of the solute.

∴ 1000 c.c. of 1 (N) acid solution = 1000 c.c. of 1 (N) alkali. Similarly 1000 c c. of 2 (N) acid solution = 1000 cc. of 2 (N) alkali solution. *Or*, x c.c. of y (N) acid solution $= x$ c.c. of y (N) alkali solution.

(3) *At the point of neutralisation,*

volume of the acid × normality of the acid
= volume of the alkali × noramlity of the alkali.

This is known as the normality equation.

Let V_1 c.c. of S_1 (N) acid solution exactly neutralise
V_2 c.c. of S_2 (N) alkali solution

Now, from the 1st. principle,

V_1 c.c. of S_1 (N) acid solution $= (V_1 \times S_1)$ c.c. of 1 (N) acid solution.

and V_2 cc of S_2 (N) alkali solution$\equiv(V_2 \times S_2)$ cc of 1 (N) alkali solution.

$\therefore$ $(V_1 \times S_1)$ cc of 1 (N) acid solution$\equiv(V_2 \times S_2)$ cc of 1 (N) alkali solution.

Since, from 2nd principle, solutions of the same normality react in equal volumes,

we have, $V_1 \times S_1 = V_2 \times S_2$

i.e., volume of the acid × its strength in normality = volume of the alkali × its strength in normality.

This rule governs all neutralisation reactions.

The volumes V_1 and V_2 are known from titration and if (S_1) the strength of acid is known, then the strength of the alkali (S_2) can be found out or vice versa.

14·7. **Preparation of standard solutions :**

When the weight of a substance present in a given volume of the solution is known it is a standard solution. That is a solution of known concentration is called a standard solution.

Substances like sodium carbonate, oxalic acid, succinic acid etc. are found in pure state and are also stable compounds. Their standard solutions can be prepared by directly weighing out the required quantity of the pure solute accurately and dissolving the same in a definite volume of the solution in a measuring flask. These are called primary standards.

But most of the acids and alkalis, such as NaOH, KOH, HCl, H_2SO_4 etc. are not available in pure anhydrous state and cannot be accurately weighed. In such cases a solution of approximate required strength is prepared and then this solution is standardised by titrating aganist a primary standard solution. From the titration result, the true strength of the solution is known— these are called secondary standards.

(1) **Preparation of 250 cc of 0·1 (N) Na_2CO_3 solution.**

The equivalent weight of $Na_2CO_3 = \frac{\text{Mol. wt.}}{2} = \frac{106}{2} = 53.$

Hence 1000 cc of 0·1 (N) Na_2CO_3 should contain 5·3 gm. Na_2CO_3

Therefore to prepare 250 cc of 0·1 (N) solution, Na_2CO_3 required = 5·3/4 = 1·325 gms.

Some pure and dry sodium carbonate taken in a weighing bottle is weighed accurately in a chemical balance. Since it is difficult and tedious time-consuming operation to weigh out exactly 1·325 gm of Na_2CO_3, a quantity very near to the required amount is transferred to the 250 c.c. measuring flask (Fig 14-2) through a funnel. The bottle is weighed again. The difference of the two weights gives the amount of Na_2CO_3 transferred ; suppose it is 1·375 gm. Now distilled water is added in small quantities through the funnel to the flask and it is well shaken to dissolve the sodium carbonate completely. The volume of the solution is then made up to the mark by carefully adding more distilled water. The last few drops should be added from a pipette so that the bottom of the meniscus coincides with the mark on the flask. The flask is closed with a glass stopper and then well shaken to get a uniform solution. The strength of the solution is not 0·1 (N).

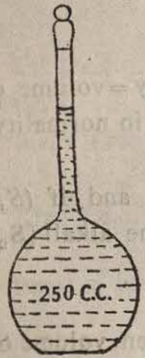


Fig. 14.2. A measuring flask

Now, 1·325 gms of Na_2CO_3 per 250 c.c. solution make just N/10 solution.

$\therefore$ 1·375 gm per 250 cc would make $\frac{1 \cdot 375}{1 \cdot 325}\left(\frac{N}{10}\right)$, i.e.,

$1 \cdot 038\left(\frac{N}{10}\right)$ solution. Hence the strength is known but it is 1·038 times stronger than $\left(\frac{N}{10}\right)$. 1·038 is called the *factor* of the solution.

$$\therefore \text{ factor} = \frac{\text{the weight of solute dissolved}}{\text{the required weight}}.$$

Now, suppose 1000 cc of this prepared solution is equivalent to x cc of $\left(\frac{N}{10}\right)$ solution. Then by the normality rule.

$$1000 \times 1 \cdot 038\left(\frac{N}{10}\right) = x \times \left(\frac{N}{10}\right).$$

$$\text{or, } x = 1038 \text{ cc}$$

This means that if 1000 c.c. of the prepared solution is diluted by adding 38 cc water, the resulting solution will be exactly decinormal $\left(\frac{N}{10}\right)$.

(ii) **Preparation of 0·1 (N) H_2SO_4 solution :–**

The equivalent weight of sulphuric acid = 49. Hence the amount required for 1 litre of 0·1 (*N*) solution = 4·9 gms. But sulphuric acid being hygroscopic and corrosive, cannot be accurately weighed. So first of all an approximately $\left(\frac{N}{10}\right)$ Solution of H_2SO_4 is prepered. From the specific gravity and and the purity of the acid supplied, the volume of it that will contain 4·9 gm. of pure sulphuric acid is calculated as follows :—

Let the specific gravity of sulphuric acid be 1·84 and its purity 96%, i.e.,

96 gm pure H_2SO_4 is present in 100 gm. of the sample

or, 4·9 gm pure H_2SO_4 is present in $\frac{100 \times 4{\cdot}9}{96}$ gm of the sample

= 5·104 gm of the sample.

Since the sp. gravity of the sample of the acid = 1·84

$\therefore$ the volume of the acid required $= \frac{5{\cdot}104}{1{\cdot}84} = 2{\cdot}77$ cc

That is to say, 2·77 cc of the given sample of H_2SO_4 contain 4·9 gms of pure acid. Hence about 2·8 cc of the sample of the acid is measured out by a graduated pipette into a litre-measuring flask and diluted with water upto the mark, and well shaken. This is approximately $\frac{N}{10}$ sulphuric acid solution.

The volume of acid to be taken in preparing one litre of approximately $\frac{N}{10}$ H_2SO_4 solution can also be calculated as follows :—

The concentrated sulphuric acid generally used in the laboratory is approximately 36(N). Suppose *x* cc of this acid would be equivalent to 1000 cc of 0·1(N) H_2SO_4 solution. Thus,

$$x \times 36\ (\mathrm{N}) \equiv 1000 \times 0{\cdot}1\ (\mathrm{N})\ \text{or, } x \approx 2{\cdot}8\ \text{cc (approx)}$$

The actual strengh of the prepared sulphuric acid solution is then determined by titrating with a 0·1(N) Na_2CO_3 solution (primary standard). 25 cc of 0·1(N) Na_2CO_3 solution is taken in a beaker by means of a pipette and diluted to about 50 cc with distilled water—one or two drops of methyl orange indicator is added to the solution, which turns yellow. The prepared acid solution is taken in a burette and added drop by drop to the alkali solution until the pink colour is just obtained at the equivalence point —the solution being carefully stirred with a glass rod during titration. The volume of the acid used up is read from the burette. Three titrations are usually done and the mean of the readings taken. Suppose 23·5 cc of the acid solution was required to neutralise 25 cc of 0·1 (N) Na_2CO_3 solution. Then if S be the strength of the prepared acid solution, we have,

$$23{\cdot}5 \times S = 25 \times 0{\cdot}1(\mathrm{N})\ \text{or}\ S = 0{\cdot}106\ (\mathrm{N}).$$

Hence the strength of the prepared H_2SO_4 solution = 0·106(N)

$$\therefore 1{\cdot}06 \left(\frac{\mathrm{N}}{10}\right).\quad (\text{factor} = 1{\cdot}06)$$

The strength being accurately known, this can be used as a secondary standard, to determine the strength of other alkali solutions.

To prepare an exact decinormal solution of sulphuric acid this solution has to be diluted to the necessary extent. Suppose x cc of this solution would be required to obtain 100 cc of 0·1 (N) H_2SO_4 solution.

Then, $x \times 0{\cdot}106(\mathrm{N}) = 100 \times 0{\cdot}1\ (\mathrm{N})$ or, $x = 94{\cdot}3$ cc

Hence, if 94·3 cc of the acid is diluted with 5·7 cc water to make the volume 100 cc the acid becomes exactly decinormal i. e. 0·1 (N).

(iii) **Preparation of a litre of 0·1 (N) NaOH solution :**

Since caustic soda is hygroscopic, its standard solution cannot be prepared by direct weighing. Equivalent weight of NaOH = 40 hence a decinormal solution will contain 4 gms of caustic soda per litre.

Approximately $\left(\frac{N}{10}\right)$ NaOH solution is first prepared by dissolving about 4 – 5 gms of NaOH, obtained by weighing in a rough balance, in a litre of water. This solution is then titrated against a standard acid solution using phenolphthalein as indicator The standard acid solution may be the H_2SO_4 acid solution as prepared earlier or may be a solution of oxalic acid or succinic acid prepared by direct weighing as primary standard.

25 cc of the alkali solution is taken in a beaker and diluted with water to about 100 cc. 1 or 2 drops of phenolphthalein is added—the solution turns pink. Standard acid solution is run drop by drop from the burette with constant stirring till the solution is just colourless at the equivalence point.

Suppose : 25 cc of the prepared NaOH solution

$$\equiv 26{\cdot}5 \text{ cc } 1{\cdot}06 \left(\frac{N}{10}\right) H_2SO_4 \text{ acid solution.}$$

Let x be the strength of NaOH solution, then

$$25 \times x = 26{\cdot}5 \times 1{\cdot}06 \left(\frac{N}{10}\right)$$

$$\therefore \quad x = 1{\cdot}124 \left(\frac{N}{10}\right).$$

Suppose p cc of this solution on dilution gives 1000 cc of $\frac{N}{10}$ caustic soda solution. or,

$$p \times 1{\cdot}124 \left(\frac{N}{10}\right) = 1000 \times \left(\frac{N}{10}\right) \quad \therefore \quad p = 889{\cdot}7 \text{ cc}$$

So, 889·7 cc of the prepared NaOH solution is transferred to a litre flask and the volume is made up to the mark, when the resulting solution will be exactly decinormal.

Numerical problems :

1. What amount of Na_2CO_3 would be necessary to prepare (a) 100 cc of 0·25 (N) solution ; (b) 200 cc of 0·25 (M) solution ; (c) 500 cc of 5% solution ? (Na = 23)

$$\text{gm equivalent of } Na_2CO_3 = \frac{106}{2} = 53 \text{ gm}$$

(a) To prepare 1000 cc of 1 N solution, 53 gm Na_2CO_3 are required.

∴ To prepare 100 cc of ·25 (N) solution, $\frac{53 \times \cdot 25}{10}$ or 1·325 gm Na_2CO_3 are required.

(b) gm. molecular wt. of $Na_2CO_3 = 106$ gm.

To prepare 1000 cc. of 1 (M) solution, 106 gm Na_2CO_3 are required

∴ To prepare 200 cc. of 0·25 (M) solution, $\frac{106 \times 200 \times \cdot 25}{1000}$ or. 5·3 gm. of Na_2CO_3 are required.

(c) To prepare 100 cc. of 5% solution, 5 gm. of Na_2CO_3 are required.

∴ To prepare 500 cc. of 5% solution, 5 × 5 or 25 gm Na_2CO_3 are required.

2. Calculate (a) the normality of 0·2 (M) $Bi(NO_3)_3$ solution (b) the moalrity of 3(N) H_2SO_4 solution and (c) molarity of NO_3^- ions in a solution containing 1·5 moles of $Cu(NO_3)_2$ in 500 cc of solution.

(a) The gm-equivalent of $Bi(NO_3)_3 = 1$ mole/3.

∴ its 1 (M) solution = 3 (N) solution, so

0·2(M) solution = 3 × ·2(N) or ·6 (N) solution.

Hence the normality of the solution is 0·6.

(b) The gm-equivalent of $H_2SO_4 = 1$ mole/2.

∴ its 1 (N) solution = ½(M) solution, and

3 (N) solution = ½ × 3(M) or 1·5(M) solution.

Hence the molarity of the solution is 1·5.

(c) 500 cc $Cu(NO_3)_2$ solution contain 1·5 moles.

∴ no. of moles per litre = 3. So the solution is 3(M).

$Cu(NO_3)_2 \rightleftharpoons Cu^{++} + 2NO_3^-$, giving 2 nitrate ions per molecule of $Cu(NO_3)_2$ ∴ the solution is $(3 \times 2) = 6$(M) or 6 molar in NO_3^- ions.

3. 500 cc of a solution contains 1 gm NaOH and 1 gm. Na_2CO_3. What is its normality ?

1000 cc. of the solution contain 2 gm NaOH and 2 gm Na_2CO_3

So, normality with respect to NaOH $= \frac{2}{40} = \cdot 05$.

and normality with respect to $Na_2CO_3 = \frac{2}{53} = \cdot 038$

$\therefore$ Total normality $= \cdot 05 + \cdot 038 = \cdot 088$.

4. Change the concentrations of the following solutions to gm/litre :

(i) 0·05 (N) Na_2CO_3 solution, (ii) 0·2(M)H_2SO_4 solution.

(iii) 1·8(N) HCl solution,

we know, concentration in gms/litre = normality (N) × eq. wt.

= molarity (M) × mol. wt.

$\therefore$ (i) 0·05(N) $Na_2CO_3 = \cdot 05 \times 53 = 2 \cdot 65$ gm/litre.

(ii) 0·2(M) $H_2SO_4 = \cdot 2 \times 98 = 19 \cdot 6$ gm/litre.

(iii) 1·8(N) $HCl = 1 \cdot 8 \times 36 \cdot 45 = 65 \cdot 61$ gm/litre.

5. (a) How much water should be added to 400 cc 1·2(N) HCl to the make the strength 1 (N) ?

(b) What will be the normality when 5 cc of 36(N) H_2SO_4 is diluted to 250 cc. with water ?

(a) Suppose v cc of water has to be added.

Then $(v+400)$ cc of 1(N) HCl solution$\equiv$400 cc of 1·2 (N) HCl solution.

or, $(v+400) \times 1 = 400 \times 1 \cdot 12$ or, $v = 80$ cc

(b) Let the normality be x (N).

Then 5 cc of 36 (N) $H_2SO_4 \equiv 250$ cc of x (N) H_2SO_4

or, $5 \times 36\,(N) = 250 \times x$ (N) or, $x = 0 \cdot 72$

6. 30 cc of 0·2(N) H_2SO_4 and 20 cc of 0·3(N) .H_2SO_4 were mixed together. What is the strength of the mixed acid solution ?

30 cc of ·2(N) $H_2SO_4 \equiv 30 \times \cdot 2$ or 6 cc of (N) H_2SO_4

20 cc of ·3(N) $H_2SO_4 \equiv 20 \times \cdot 3$ or 6 cc of (N) H_2S_4

volume of the mixed solution $= 30 + 20 = 50$ cc., let the strength be x (N)

$\therefore$ $50 \times x(N) \equiv 12 \times 1(N)$ $\therefore$ $x = \frac{12}{50}(N)$ or 0·24(N)

7. How much $CaCO_3$ would be necessary to completely neutralise 25 cc. of 0·225(N) H_2SO_4 ?

25 cc of ·225 (N) $H_2SO_4 \equiv 25$ cc. of ·225(N) $CaCO_3$

Now 1000 cc. of (N) $CaCO_3 \equiv 50$ gm. of $CaCO_3$

(eq. wt. of $CaCO_3 = \frac{100}{2}$)

$$\therefore \quad 25 \text{ cc of } \cdot225\,(\text{N})\ CaCO_3 \equiv \frac{50\times25\times\cdot225}{1000} \text{ gm } CaCO_3$$

$$= 0\cdot281 \text{ gm.}$$

8. 25 cc of $\frac{N}{10}$ HCl neutralised 21 cc. of Na_2CO_3 solution. How much water must be added to 1 litre of the latter in order to make it exactly decinormal ?

Let x be the strength of Na_2CO_3 solution.

$$\therefore \quad 25 \text{ cc of } \left(\frac{N}{10}\right) HCl \equiv 21 \text{ cc of } x\ Na_2CO_3$$

$$\text{or,} \quad 25\times\frac{N}{10} = 21\times x \quad \therefore \quad x = 1\cdot1905\left(\frac{N}{10}\right)$$

Now, Let v cc water be added, so we have,

$$1000 \text{ cc. of } 1\cdot1905\left(\frac{N}{10}\right) Na_2CO_3 \text{ solution}$$

$$\equiv (1000+v) \text{ cc. of } \left(\frac{N}{10}\right) Na_2CO_3 \text{ soln.}$$

$$\text{or,} \quad 1000\times1\cdot1905\left(\frac{N}{10}\right) \equiv (1000+v)\times\left(\frac{N}{10}\right)$$

$$\therefore \quad v = 190\cdot5 \text{ cc.}$$

9. 50 cc of a NaOH solution is neutralised by 36 cc of 0·36 (N) HCl solution. Calculate the normality of the caustic soda solution. Estimate the quantity of NaOH present in 100 cc of the solution.

Let x be the strength in normality.

$$\therefore \quad 50\times x\,(\text{N}) = 36\times\cdot36\,(\text{N}) \qquad \therefore \quad x = 0\cdot2592\,(\text{N})$$

$$\therefore \quad \text{gm of NaOH per litre} = \cdot2592\times40 \quad (40 = \text{eq wt. of NaOH})$$

$$\therefore \quad \text{gr. of NaOH in 100 cc.} = \frac{\cdot2592\times40}{10} = 1\cdot0368 \text{ gm.}$$

10. 2·24 gm. of a dibasic acid was dissolved in water and the solution diluted to 250 cc ; 25 cc of this solution required 40 cc of 1·24 $\frac{N}{10}$ alkali for neutralisation. Calculate the equivalent and molecular wts. of the acid.

Let the strength of the acid solutiou be x.

$\therefore\ 25 \times x = 40 \times 1{\cdot}24\left(\frac{N}{10}\right)$; $\therefore\ x = 1{\cdot}984\left(\frac{N}{10}\right)$

250 cc of $1{\cdot}984\ \left(\frac{N}{10}\right)$ acid solution contain 2·24 gm acid

or, 250 cc of ·1984(N) acid solution contain 2·24 gm acid

$\therefore$ 1000 cc of 1 (N) acid solution contain $\frac{2{\cdot}24 \times 4}{{\cdot}1984}$ gm.

or, 45·16 gm

$\therefore$ the eq. wt. of the acid = 45·16 and

the mol. wt. of the acid = $45{\cdot}16 \times 2 = 90{\cdot}32$.

11. 25 cc of an alkali solution was mixed with 8 cc of a 0·75 (N) acid solution and for complete neutralisation it further required 15 cc of a 0·8 (N) acid solution. Find the strength of the given alkali solution.

8 cc. of 0·75 (N) acid solution $\equiv 8 \times {\cdot}75$ or, 6 cc of 1 (N) acid soln.

again, 15 cc of 0·8 (N) acid soln $= 15 \times {\cdot}8$ or 12 cc. of 1 (N) acid solution.

$\therefore$ Total acid = 18 cc of 1 (N) soln.

Let x be the strength of the given alkali solution.

Then, $25 \times x = 18 \times 1$ (N) $\therefore\ x = \frac{18}{25} = 0{\cdot}72$ (N).

12. A specimen of limestone contain 60% $CaCO_3$. Calculate the amount of stone which will be required to generate just sufficient CO_2 to convert 1 litre of (N) NaOH solution into sodium carbonate. Formula weight of NaOH = 40, and that of $CaCO_3$ = 100.

1 litre (N) NaOH solution = 1 gm equivalent of NaOH

= 1 mole of NaOH.

From the equations $2\ NaOH + CO_2 = Na_2CO_3 + H_2O$

and $CaCO_3 = CaO + CO_2$

2 moles of NaOH = 1 mol of CO_2 = 1 mole of $CaCO_3$,

$\therefore$ 1 mole of NaOH = 0·5 mole of $CaCO_3$ = 50 gm of $CaCO_3$

But limestone contains only 60% $CaCO_3$.

$\therefore$ wt. of stone required $= \frac{100}{60} \times 50 = 83{\cdot}33$ gm.

OR, 1 litre of (N) NaOH solution contains 40 gms of NaOH.

$$2\,NaOH + CO_2 = Na_2CO_3 + H_2O$$

80 gms of NaOH react with 44 gms of CO_2

$\therefore$ 40 grm of " " " 22 " " "

Now $CaCO_3 = CaO + CO_2$

44 gms of CO_2 are obtained from 100 gms of $CaCO_3$

$\therefore$ 22 gms of CO_2... .... 50 gms of $CaCO_3$.

But lime stone contains only 60% $CaCO_3$; hence 50 gms of $CaCO_3$ are present in $\frac{100 \times 50}{60} = 83{\cdot}33$ gm of lime stone.

13. One gm of a mixture of Na_2CO_3 and $NaHCO_3$ was dissolved in 250 cc water. 25 cc of this solution required 15 cc. of $\left(\frac{N}{10}\right)$ HCl solution for neutralisation, Find the percentage of bicarbonate in the mixture.

Suppose the mixture contained x gm $NaHCO_3$. The amouut of Na_2CO_3 was $(1-x)$ gms.

Now 25 cc of the given solution $= 15$ cc of $\left(\frac{N}{10}\right)$HCl.

$\therefore$ 250 cc of the given solution $= 150$ cc of $\left(\frac{N}{10}\right)$ HCl

$= 15$ cc of 1 (N) HCl.

1000 cc of 1 (N) HCl contains 1 gm. equivalent or 36·5 gm HCl.

$\therefore$ 15 cc of 1 (N) HCl contain $\frac{36{\cdot}5 \times 15}{1000}$ or, 0·5475 gm HCl.

Now, $NaHCO_3 + HCl = NaCl + H_2O + CO_2$

$$\begin{array}{ll} 84 & 36{\cdot}5 \text{ gm} \\ x & \frac{36{\cdot}5 \times x}{84} \text{ gm.} \end{array}$$

Again $Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O$

$$\begin{array}{ll} 106 & 73 \text{ gm} \\ (1-x) & \frac{73\,(1-x)}{106} \text{ gm,} \end{array}$$

∴ 1 gm mixture consumed $\frac{36{\cdot}5x}{84}+\frac{73\,(1-x)}{106}$ gm acid

or, $\frac{36{\cdot}5x}{84}+\frac{73\,(1-x)}{106}=0{\cdot}5475$

Solving $x=0{\cdot}5549$ gm. Hence the bicarbonate in the mixture is 55·49%.

14. 0·21 gm of a metal was added to 100 cc of 0·5 (N) H_2SO_4. After dissolution, the exccss acid required 32·5 cc of 1 (N) alkali solution. What is the equivalent weight of the metal ?

100 cc of the acid solution≡32·5 cc of 1 (N) alkali soln.

≡32·5 cc of 1 (N) H_2SO_4 left unused.

volume of acid taken = 100 cc 0·5 (N) H_2SO_4≡50 cc of 1 (N) H_2SO_4

∴ volume of the acid reacting with the metal = (50 − 32·5) or, 17·5 cc (N) H_2SO_4

17·5 cc of (N) H_2SO_4 react with 0·21 gm of the metal

∴ 1000 cc. of (N) H_2SO_4 react with $\frac{{\cdot}21\times1000}{17{\cdot}5}$ gm. or 12 gm of the metal

∴ the equivalent weight of the metal = 12.

15. What volume of pure NH_3 at 27°C and 750 mm would be obtained from 10 gms of NH_4Cl ? What volume of $\left(\frac{N}{10}\right)H_2SO_4$ would be neutralised by this NH_3 ?

10 gms of $NH_4Cl=\frac{10}{53{\cdot}5}$ gr eq. of NH_4Cl

$=\frac{10}{53{\cdot}5}\times22{\cdot}4$ litres of $NH_3=4{\cdot}1869$ litres of NH_3 at N.T.P.

∴ V = volume at 27°C and 750 mm.

$$=\frac{4{\cdot}1869\times760\times300}{750\times273}=4{\cdot}662 \text{ litres.}$$

Again 4·1869 litres of NH_3 at NTP $=\frac{4{\cdot}1869}{22{\cdot}4}$ moles of NH_3 at NTP.

$\equiv\frac{4{\cdot}1869}{22{\cdot}4}$ gm eq. of $NH_3\equiv\frac{4{\cdot}1869}{22{\cdot}4}$ gr. eq. of H_2SO_4

$\equiv\frac{4{\cdot}1869\times49}{22{\cdot}4}$ gm of H_2SO_4.

Now, 4·9 gm H_2SO_4 are present in 1 lit of $\left(\frac{N}{10}\right)$ acid.

$$\therefore \ \frac{4{\cdot}1869\times49}{22{\cdot}4} \text{ gm } H_2SO_4 \text{ are present in } \frac{1\times4{\cdot}1869\times49}{4{\cdot}9\times22{\cdot}4}$$

$$\text{lit. of } \left(\frac{N}{10}\right)\text{acid} = 1{\cdot}87 \text{ lit.}$$

Exercises—14

1. Define with suitable examples the following terms.
   (a) Neutralisation
   (b) Indicator
   (c) Standard solution

2. What is an acid-base indicator ? What indicators are used in titrating (i) ammonia with sulphuric acid, (ii) caustic soda with acetic acid ? and (iii) caustic potash with hydrochloric acid ? State reasons for the choice of your indicators ?

3. What are meant by primary and secondary standard for neutralisation studies ? How do you prepare a standard for neutralisation studies ? How do you prepare a standard (N/10) H_2SO_4 solution ?

4. What is a normal solution ? How does it differ from a molar solution ? In which case these two are the same ? What is normality factor ?

5. Justify or modify the following statements :—
   (i) 10 cc. of 5 % NaOH solution exactly neutralise 10 cc. of 5 % HCl soln.
   (ii) Indicator takes part in the neutralisation reaction and that is why its colour changes.
   (iii) The reaction of an acid with equivalent quantity of a base gives a solution which is always neutral.

6. What amounts of Na_2CO_3 will be required to prepare :
   (i) 250 cc of 0·5 (N) Na_2CO_3
   (ii) 500 cc. of 0·5(M) Na_2CO_3
   (iii) 1000 cc. of 5 % Na_2CO_3 [(i) 6·625 gm, (ii) 26·5 gm, (iii) 50 gm]

7. How much water should be added to each of the following so as to make the strength of I (N) ?
   (i) 33 cc. 1·8(N) H_2SO_4 (ii) 1200 cc. 1·5(N) NaOH (iii) 400 cc. of 1·4(N) HCl [(i) 26·4 cc., (ii) 600 cc., (iii) 160 cc.,]

8. 25 cc. of 0·1(N) NaOH solution neutralises 22·5 cc. of a HCl solution. How much water is to be added to 500 cc. of the HCl solution to make it 0·1(N) [55 cc.]

9. 50 cc. of 0·8% NaOH solution is mixed with 25 cc. of 0·5(N) HCl solution. What wil be the acidic or alkaline normality of the mixed solution ? [acidic ; 0·033(N)]

10. 30 cc. of 0·32(N) HCl is mixed with 20 cc. of 0·45(N) NaOH.

(i) Find out if the mixture would be acidic or alkaline.

(ii) What would be the normality of the acid or alkali present in the mixture ?

(iii) Estimate the normality of the mixture in respect of the salt present in it. [(i) acidic, (ii) 0·012(N), (iii) 0·18(N)]

11. 22 cc. of $\frac{N}{2}$ H_2SO_4 neutralised 20·6 cc of KOH solution. How much water must be added to 1 litre of the latter to make it exactly (N/2) ? [68 cc.]

12. Calculate (i) the molarity of 1·5(N) $Al_2(SO_4)_3$ solution, (ii) the normality of 0·5(M) H_3PO_4 solution (iii) the molarity of Al^{3+} ions in a solution made by dissolving 17·1 gm of $Al_2(SO_4)_3^-$ (formula weight 342) in 500 cc, of water. [(i) 0·25(M), (ii) 1·5(N), (iii) 0·2(M)]

13. 20 cc. N/10 solution of HNO_3 is neutralised by 2·25 cc, Na_2CO_3 solution. Calculate the strength of the carbonate solution in terms of normality and the weight of the carbonate per litre of the solution. [0·089 (N), 4·72 gm]

14. 20 cc. 1(N) HCl solution is mixed with 120 cc. (N/4) H_2SO_4'' solution. What volume of 0·33(N) KOH solution will be required to neutralise the acid mixture ? [151·5 cc.]

15. A sample of sulphuric acid contains 22·% H_2SO_4 by weight and its density is 1·16 gm/cc. Find the normality of the acid solution. [5·257 (N)]

16. What will be the normality, when

(a) 38 cc. of 16(N) HNO_3 is diluted to 100 cc. with water,

(b) 500 mgm. H_2SO_4 is present in 45 cc. solution.

[(a) 6·08(N), 0·227(N)].

17. Equal weights of KOH and NaOH are separately neutralised by a given acid solution. In which case would more acid be required ? [In case of NaOH].

18. Equal weighs of NaOH and Na_2CO_3 are separately dissolved in equal volumes of solutions. Compare the strengths of the two solutions. [5·3 : 4].

19. One litre of a solution contains 2 gm KOH. How much NaOH should be added to it to make the strength of the alkali soltion 0·05 (N) ? [0·571 gm].

20. To 50 cc. of a solution of HCl 25 cc. of 0·82(N) NaOH solution were added. The excess of the acid in the solution required 30 cc. of 0·09(N) Na_2CO_3 solution for neutralisation. What was the normality of the acid solution ?

[0·464 N].

21, Two gm. of an impure sample of Na_2CO_3 was dissolved in 500 cc. of water. To 50 cc. of this solution added 50 cc. of (N/10) HCl. The excess acid required 10 cc. 0·16(N) NaOH solution for neutralisation. Calculate the purity of the Na_2CO_3 sample. [90·1% Na_2CO_3]

22. 2·835 gm of a dibasic acid (M=126) was dissolved in 500 cc. of water. 22·5 cc. of this acid solutiou was neutralised by 25 cc. of a caustic soda solution. 10 cc. of the same cauatic soda solution can also neutralise 8·0 cc. of a sulphuric acid solutson. Find out the normality of the sulphuric acid solution.

[0·101 (N)]

23. 0·12 gm of a metal dissolved in 25 cc. of $\left(\frac{N}{2}\right)$ HCl. The excess acid required 25 cc. of (N/10) NaOH for neutralisation. What is the equivalent weight of the metal ? [12]

24. Estimate the volums of 1·12 (N) NaOH solution which would neutralise a mixture of 30 cc. 2(N) H_2SO_4 solution and 40 cc. 0·5(N) H_2SO_4 oslution.

[71·4 cc.]

25. 0·5 gm potassium bicarbonate required 20 cc. 0·25 (N) HCl for neutralisation. What is the equivalent weight of potassium bicarbonate ? [100].

26. Calculate the volume of 0·1(N) HCl solution which would netralise the lime produced from 1 kg of $CaCO_3$. [200 lit.]

27. A solution containing 0·315 gm. of a dibasic acid was neutralised by 41·7 cc. of 1·2 (N/10) caustic soda solution. Find the molcular weight of the acid.

[126]

28. 10 cc. of conc. H_2SO_4 (sp. gr. 1·83) was diluted to a litre, 20 cc. of this solution reqired 28 cc of 0·25 (N) Na_2CO_3 solution. Calculate the percentage of H_2SO_4 in the original acid. [93·71%]

29. 5·6 litrer of dry ammonia gas at N.T.P. was led into a litre of normal H_2SO_4 solution. What volume of 0·1(N) KOH would be now necessary to neutralise the mixture. [7·5 litre].

30. Two gram of sample of NH_4Cl contaminated with NaCl is mixed with 50 cc. of 1(N) NaOH solution and the solution is boiled till there is no change of colour of a moist red litmus paper held in the vapour. The solution after cooling requires 20 cc. of 1(N) H_2SO_4 for neutralisation. What was the percentage of NH_4Cl in the sample ? [80·25%]

31. 2·95 gm of a dibasic acid was dissolved in water and the solution diluted to 250 cc. ; 25 cc. of this solution was neutralised by 25 cc. of N/5 Na_2CO_3 solution. Calculate the eq. wt. and mol. wt. of the acid. [59, 118]

32. 1·5 gms. of a mixture of Na_2CO_3 and $NaHCO_3$ were dissolved in 250 cc. water. 25 cc. of the solution required 27 cc. of (N/10) HCl for neutralisation. Find the composition of the mixture. [1·313 Na_2CO_3, ·187 $NaHCO_3$]

33. 0·02 gm. of a matal after solution in water produced an alkali which was neutralised by 10 cc of (N/10) HCl solution. Find the eqnlvalent wt. of the metal. [20]

34. A specimen of chalk contain calcium sulphate as impurity. One gram of the solid was allowed to be in contact with 230 cc of (N/10) HCl solution. The excess of acid in the mixture was completely neutralised by 8·0 cc of 0·45 (N) NaOH solution. Calculate the prercentage of chalk in the sample. [97%]

35. 1·054 gm of a carbonate of a bivalent metal is dissolved in 50 cc (N) HCl and the excess of acid is neutralised by 25 cc (N) caustic soda. Find the eq. wt. and at wt. of the metal. [12·16, 24·32]

36. A solution contained Na_2CO_3 and $NaHCO_3$. 25 cc of the solution required 5 cc of (N/10)HCl for neutralisation, using phenaopthalein as indicator ; methyl orange was then added, when a further 15 cc of acid was required. Calculate the amount of each salt in the given solution per litre. [Na_2CO_3=2·12 gm ; $NaHCO_3$=3·36 gm]

37. 1 gm. of a mixture of sodium and potassium carbonate needs 19·7 cc of HCl containing 0·03 gm. of acid per cc. What is the weight of each carbonate present ? (K=39·0) [K_2 CO_3=0·616 gm. Na_2 CO_3=0·384 gm]

38. If 1 gm. of anhydrons sodium carbonate were added to 20 cc of a normal solution of sulphuric acid, what volume of CO_2 would be set free at N.T P. ? Would the resulting solution be acidic or alkaline ? What volume of (N/10) acid or alkali would be required to neutralise it ?
[acidic ; 11·3 cc of N/10 alkali ; CO_2 formd=211·3 cc]

39. An excess of ferrous sulphide is added to 125 cc of dilute Sulphuric acid and the volume of hydrogen sulphide set free measured 560 cc at O°c and 760 mm. Calculate the normality of the acid. [0·4 (N)]

40. In what proportion of volumes of two acid solutions of strengths 0·25 (N) and 0.4 (N) respectively should be mixed, so that the strength of the resulting mixed solution will be 0·32 (N) ? [8 : 7]

41. Two acids A and B are titrated separately ; each time 25 cc of (N)Na_2 CO_3 solution require 10cc and 40 cc respectively of their solution for complete neutralisation. What volumes of A and B would you mix to produce 1 litre of (N) acid solution ? [200 cc A + 800 ce B]

42. 0·2815 gm $CaCO_3$ is dissolved in 30 cc 1(N) HNO_3. The excess of acid requires 24·45 cc of 1(N) NaOH. Calculate the percentage of CO_2 in the sample of $CaCO_3$. [43·53%]

43. In what volumetric proportion should an acid of 0·6 (N) be added to an alkali solution of strength 0·4(N) to make the resulting solution (i) neutral, (ii) an acidic solution of strength 0·2(N), (iii) an alkaline solution of strength 0·2(N). [2 : 3, 3 : 2, 1 : 4]

44. What volume of a 5% Na_2CO_3 solution will be required to neutralise a lire of (N/10) sulphuric acid ? [106 cc]

45. 2 gms. of a mixture of carbonate, bicarbonate and chloride of sodium gave on gentle heating till no further evolution of gas occured, 62 cc of CO_2 at 36°c and 752 mm. pressure, 1·6 gm. of same mixture required 26 cc of (N) HCl for complete neutralisation. Calculate the composotion of the mixture. [$Na_2CO_3 = 72 \cdot 85\%$, $NaHCO_3 = 21\%$, $NaCl = 6 \cdot 15\%$]

CHAPTER—XV

CHEMICAL EQUILIBRIUM : THE LAW OF MASS ACTION

From actual experiments it has been observed that many chemical changes do not go to completion. The reactions are found to be apparently stopped after proceeding to a certain extent. A portion of the reactants, sometimes a considerable portion, remain unaltered in the system. In this chapter we shall study the answer to the question, "how far a reaction would go" ?

15.1. **Reversible and Irreversible changes :**

In many chemical reactions, it is found that the products of the change can react amongst themselves and reproduce the original reactants. That is, such reaction can proceed in both ways. If one is called the "forward reaction", the opposite one is called the "backward or reverse reaction". Thus, when steam is passed over heated iron in a tube, steam is decomposed by red hot iron resulting in the formation of magnetic oxide of iron, Fe_3O_4 and hydrogen. The equation for the reaction is $3Fe+4H_2O \rightarrow Fe_3O_4 +4H_2$. At an earlier time, it would have been said that iron has a greater affinity for oxygen than does hydrogen. However, under the same condition, if hydrogen is passed over heated magnetic oxide of iron, the latter will be reduced to iron and steam is formed : $Fe_3O_4+4H_2 \rightarrow 3Fe+4H_2O$. Evidently the affinity of iron or hydrogen for oxygen does not explain such chemical changes, for one reaction is the reverse of the other.

The reactions in which such opposite processes take place are called "*reversible reactions*". *A reversible reaction is one in which the poducts formed from starting materials can react to reform these original substances.* Such reactions are repersented with a double arrow "$\rightleftharpoons$" notation ;

$$3Fe+4H_2O \rightleftharpoons Fe_3O_4 +4H_2$$

The reaction proceeds to completion when steam is passed over heated iron in an open tube because the excess steam carried off the hydrogen and thereby prevent the reverse action that would take place between hydrogen and iron oxide. For a similar reason, iorn oxide is completely reduced by an excess of hydrogen to iron and steam. However, if water and iron are heated in a closed container, the same reaction sets in ; but it seems to stop before completion. The exaplanation of this behaviour is that the hydrogen and iron oxide, formed by the first reaction, are now, interacting and forming the initial substances, water and iron. Both reactions are proceeding, each undoing the effect of the other. In a reversible reaction, if one or more products deposit as a precipitate owing to insolubility or pass into gaseous state due to their volatility and are thereby removed from the system, the reversibility is not possible. Examples of common reversible reactions are—

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$

$H_2 + I_2 \rightleftharpoons 2HI$

$NH_4Cl \rightleftharpoons NH_3 + HCl$

$N_2 + O_2 \rightleftharpoons 2NO$

$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$

$2SO_2 + O_2 \rightleftharpoons 2SO_3$

$N_2O_4 \rightleftharpoons 2NO_2$ etc., etc.,

There are cases where the extent of the reverse reaction is practically negligible so that these appear to proceed completely in one direction. These are called *"irreversible reaction"*. A reaction in which the products do not interact to form the original materials is, therefore, said to be **irreversible**. Such reactions are generally found in some of the decomposition, neutralisation, precipitation processes. Examples are—

$HCl + NaOH \rightarrow NaCl + H_2O$

$2KClO_3 \rightarrow 2KCl + 3O_2$

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$

$2H_2O_2 \rightarrow 2H_2O + O_2$ etc. etc.

Theoretically, however, all reactions are reversible and certain reactions which appear to be irreversible are due to our inability to produce the right experimental conditions to run such reactions in the reverse way.

15.2. The chemical Equilibrium :

Let us now try to picture what happens in a reversible reaction. Consider the classical reaction between equimolar amounts of hydrogen and iodine vapour when heated in a closed vessel at 400°C. : $H_2+I_2 \rightleftharpoons 2HI$. It is evident that at first no reaction other than that between hydrogen and iodine is possible as there will be no product present in the system. But as the reaction proceeds, more and more hydrogen iodide accumulates in the vessel and the reverse reaction starts, the HI molecules now begin to decompose into its constitutent elements, hydrogen and iodine. So both the forward reaction and the backward reaction would proceed side by side, the rate of the former gradually decreases and that of the latter increases with time. After sometime a state will be reached when all the three substances, hydrogen, iodine and hydrogeniodide coexist in a state of balanced activity. At this point it has been found that about 80 percent of the H_2-I_2 mixture has been converted into hydrogen iodide, 20% of the mixture remains unchanged, and their amounts will remain unaltered for unlimited time. Such a state of chemical reaction is called *equilibrium state.* At this state the two opposing reactions go on at equal rates so that as much HI is formed as is decomposed in given time, there is actually no ceasation of either reaction. All reversible reactions lead to this condition of apparently suspended action—a condition of chemical equilibrium. Such a condition is said to be a state of dynamic equilibrium, not a statically balanced one. The same state of equilibrium is obtained whether one starts with a mixture of hydrogen and iodine or with pure hydrogen iodide. If pure HI is heated in a closed vessel at the same temperature of 400°C, 20% of it is found to be decomposed, 80% HI remains in equilibrium

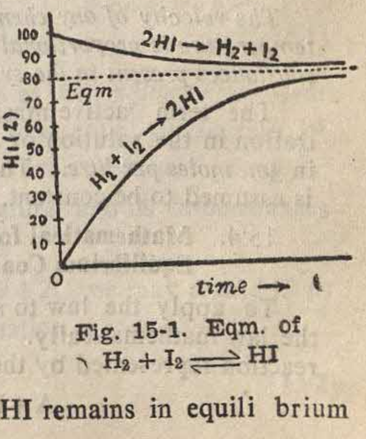


Fig. 15-1. Eqm. of $H_2 + I_2 \rightleftharpoons HI$

with 20% of H_2-I_2 mixture. The attainment of quilibrium of the H_2-I_2 reaction has been graphically shown in Fig 15-1. The point of such an equilibrium varies only with temp. The attainment of chemical equilibrium reveals the following facts ;

(1) the equilibrium can be reached from either direction.

(ii) the concentrations of the participants attain a fixed value at equilibrium and

(iii) the reaction cannot be complete (100%) in either direction.

These indeed are three characteristics of a reversible reaction attaining equilibrium.

15.3. The Law of mass Action :

The attainment of the state of equilibrium depends on the speed of a reaction, the relative rates of the two opposing reactions determine the point of eqilibrium. Hence the factors which control the rates of reactions will also control the point of equilibrium. The principal factors which determine the velocity or the rate of a chemical reaction are (i) concentration (or pressure for gaseous reactions), (ii) temperature, and (iii) catalysts. The effect of concentrations (relative masses) of the reacting substances on the reaction rate was studied thoroughly by two Norwegian chemists, Guldberg and Waage, who enunciated the famous *law of mass action* in 1864. A quantitative relationship between the relative masses of products and of the reactants of a chemical reaction was established with the help of this law which states as follows :—

The velocity of any chemical reaction at any instant at a given temperature is proportional to the active mass of each of the reacting substances present in the system at that instant.

The term 'active mass' of a reactant means its molar concentration in the solution or in the gas phase. Usually it is expressed in gm *moles per litre*. The 'active mass' of a solid or a pure liquid is assumed to be constant.

15·4. Mathematical formulation of the law of Mass Action : Equilibrium Constant.

To apply the law to specific cases it is necessary to formulate the law mathematically. Let us take a simple case of a reversible reaction represented by the equation—

$$A+B \rightleftharpoons C+D.$$

Now, at the begining of the reaction, there will be present only the reactants A and B without any of the products C and D. According to the law of mass action, the rate of the forward reaction R_{AB} is proportional to the concentrations of A as well as of B. If C_A and C_B be the molar concentrations of A and B respectively, then

$$R_{AB}=k_1C_AC_B$$

Where k_1 is a constant called the velocity constant for the direct or forward reaction. As the reaction is reversible, the products of the reaction C and D which are formed would also react to produce back A and B. If C_C and C_D be the molar concentrations of C and D respectively, then the rate of the backward reaction is

$$R_{CD}=k_2C_C \,.\, C_D.$$

Where k_2 is a constant called the velocity constant of the backward reaction.

With progress of time, the concentrations of A and B decrease, and hence the rate of the forward reaction R_{AB} continuously diminishes. On the other hand, with time more and more C and D are formed. hence the rate of the backward reaction R_{CD} increases with time. At equilibrium, the rate of the forward reaction will be equal to the rate of the backward reaction i.e. at equilibrium $R_{AB}=R_{CD}$

Hence $k_1[A][B]=k_2[C][D]$, where [A], [B], [C], [D] represent the equilibrium concentrations.

$$\text{or, } \frac{[C]\,[D]}{[A]\,[B]}=\frac{k_1}{k_2}=K_C \text{ (constant)} \qquad ...[15.1]$$

Where K_C is a constant and is known as the *equilibrium constant* or *mass law constant* of the reaction. It is equal to the ratio of velocity constants of the forward and the backward reactions. It remains constant at a given temperature and its value changes with temperature.

If the reaction be of the type $2A \rightleftharpoons B+2C$, we may regard it as $A+A \rightleftharpoons B+C+C$. and the mass law equation becomes,

$$K=\frac{[B]\,[C]\,[C]}{[A]\,[A]}=\frac{[B]\,[C]^2}{[A]^2} \qquad ....[15{\cdot}2]$$

It shows that the coefficients (i.e. the number of moles) in the stoichiometric equation become the powers (or index) of the respective concentrations in the expression of the equilibrium constant. Thus, in the general case, if the reaction is represented by

$$aA + bB + ... \rightleftharpoons lL + mM + ...$$

$$\text{the equilibrium constant, } K_c = \frac{[L]^l \times [M]^m \times ....}{(A)^a \times (B)^b \times ....} \quad ... [15{\cdot}3]$$

Where the third bracket [ ] represents the concentration of the respective substances present at equilibrium.

This equation, which is the most generalised mathematical expression for the law of mass action, may be stated as follows :—

At a constant temperature, when equilibrium is reached, the product of the concentrations of the substances formed in a reversible reaction, each raised to a power equal to the coefficient of its formula in the stoichiometric equation, divided by the product of the concentrations of the reacting substances, each raised to a power equal to the coefficient of its formula in the chemical equation, is constant, and is known as the "equilibrium constant" K_c of the reaction.

This may be called the "Law of chemical equilibrium." To illustrate the law :

Reaction	Equilibrium constant
(a) $H_2 + I_2 \rightleftharpoons 2HI$	$K_c = \frac{[HI]^2}{[H_2][I_2]}$.
(b) $N_2 + 3H_2 \rightleftharpoons 2NH_3$	$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$.
(c) $4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$	$K_c = \frac{[Cl_2]^2 [H_2O]^2}{[HCl]^4 [O_2]}$.

The equilibrium constant, K_c, is a characteristic of the reaction and has a fixed value as long as the temperature remains constant. The initial concentrations of the reactants may be different, but the system would adjust in such a way that equilibrium concentrations would make the value of K_c the same, provided the temperature remains constant.

15·5. The relationship between K_c and K_p :

The equilibrium constant K_c has been expressed in terms of concentrations (gm. mole/litre) of the participents (eqn. 15·3). In the case of a gaseous equilibrium, the reactants and the products are often measured and expressed in terms of their partial pressures in the mass law equation, since the concentration of a gas is proportional to its partial pressure. So, in gaseous reactions, equilibrium constant Kp is given in terms of partial pressures. Thus.

for a gaseous reaction : $aA+bB \rightleftharpoons cC+dD$

$$K_c=\frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} .$$

$$\text{and } K_p=\frac{p_C{}^c \times p_D{}^d}{p_A{}^a \times p_B{}^b} \qquad \text{....(15·4),}$$

where p = terms represent the partial pressures of the participants.

This equilibrium constant K_p, is not necessarily the same as the other constant K_c obtained by using the concentrations, but when there is little chance of confusion the symbol K is generally used.

The relationship between K_p and K_c can be easily deduced. According to the gas law, we have.

the partial pressure p of an ideal gas at any temperature T is $pV=nRT$ and so $p=\frac{n}{V}RT=CRT$, where C is the concentration, i,e. in the present notation.

$p_A=[A]RT$. $p_B=[B]RT$ and so on. Substituting this value of p in the definition of K_p (Eqn. 15·4) for the general reaction, we get,

$$K_p=\frac{p_C{}^c \times p_D{}^d}{p_A{}^a \times p_B{}^b}=\frac{[C]^c \times (RT)^c \times [D]^d \times (RT)^d}{[A]^a \times (RT)^a \times]B]^b \times (RT)^b}$$

$$=\frac{[C]^c \times [D]^a}{[A]^a \times]B]^b} \times (RT)^{(c+d)-(a+b)}$$

$$\therefore \quad K_p=K_c.(RT)^{\Delta n} \qquad \text{....[15·5]}$$

Where Δn = (no. of moles of products) − (no. of moles of reactants) = increase in the number of moles during the reaction.

Hence if $\triangle n = 0$, i,e. the total no. of moles of reactants are equal to total no. of moles of products, K_p will be equal to K_c. In other cases $K_p \neq K_c$. In calculating the values of K, concentrations are usually expressed in moles per litre and partial pressures in atmosphere, and hence R in litre atmosphere.

Example : K_c for the reaction, $N_2 + 3H_3 \rightleftharpoons 2NH_3$ at 400°C is 0·499. Calculate K_p.

Here, $\triangle n = 2-(1+3) = -2$: $R = {\cdot}082$ lit. atm. : $T = 673°A$

$\therefore\ K_p = 0{\cdot}499 \times ({\cdot}082 \times 673)^{-2} = 1{\cdot}64 \times 10^{-4}$.

15·6. Application of the law of Mass Action :

In applying the law to specific reaction, it is to be noted that the law does not help in any way to find out independently the extent of a chemical reaction from a given amount of the reactants. It is possible to calculate the position of equilibrium for any initial concentrations of the reacting substances only when the value of K, the equilibrium constant for the reaction is already experimentally determined with a particular proportion. Let us consider the equilibrium state of some homogeneous gaseous and liquid systems to investigate how far the equations derived on the basis of the law of mass action agree with experimental data. Since the chemical transformations are reversible and proceed upto a certain extent when equilibrium is reached, the equilibrium constants are calculated in terms of the extent of chemical transformation

Equilibrium in gaseous systems :—

Example 1. Formation of hydrogen iodide from its elements :

$$\begin{array}{llll} H_2 & + \; I_2 & \rightleftharpoons 2HI. & \\ a & \quad b & \quad o & \text{....... gr. moles present in the system initially} \\ a-x & \quad b-x & \quad 2x & \text{.......gr. moles present at equilibrium} \end{array}$$

Let 'a' moles of hydrogen and 'b' moles of iodine be heated in a vessel of volume v. If x moles out of a moles of hydrogen react to form hydrogen iodide at equilibrium, then the equilibrium mixture will contain $2x$ moles of hydrogen iodide. Therefore, the number of moles of hydrogen and iodine left unreacted at equilibrium are respectively $(a-x)$ and $(b-x)$.

$\therefore$ Total no. of gm. moles present in the system.

$$=a-x+b-x+2x=a+b.$$

Let P stands for total pressure, then at equilibrium we have,

Components	Molar Concentration	Partial pressure
H_2	$\frac{a-x}{v}$	$\frac{a-x}{a+b}.P$
I_2	$\frac{b-x}{v}$	$\frac{b-x}{a+b}.P$
HI	$\frac{2x}{v}$	$\frac{2x}{a+b}.P.$

Substituting these values in the mass law equation, we have

$$K_c=\frac{[HI]^2}{[H_2][I_2]}=\frac{(2x/v)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}=\frac{4x^2}{(a-x)(b-x)}\text{ and}$$

$$K_p=\frac{p^2_{HI}}{p_{H_2}\times p_{I_2}}=\frac{(2x/a+b)^2\,P^2}{\left(\frac{a-x}{a+b}.P\right)\left(\frac{b-x}{a+b}.P\right)}=\frac{4x^2}{(a-x)(b-x)}.$$

Here the equilibrium constants K_p and K_c are the same $(\Delta n=0)$. The term v or P cancels out and therefore, does not appear in the expression which determines the value of K_p or K_c. Therefore, neither Kp nor K_c depend on the total pressure or the volume of the system. The yield of HI will be the same at whatever pressure the operation is carried out. Now, starting with equal number (a) of moles of the reactants, we have :

$$Kp=K_c=\frac{4x^2}{(a-x)(a-x)}=\frac{4x^2}{(a-x)^2}$$

This reaction has been experimentally studied by Bodenstein (1899). Known amounts of hydrogen and Iodine are heated together in various proportions in sealed tubes to a temperature of 444°C (boiling sulphur). After a time sufficiently long for equilibrium, the tubes are suddenly cooled and the amounts of hydrogen, iodine and hydrogen iodide remaining at equilibrium are analysed. Substituting these amounts in the mass law equation, equilibrium constant K_p has been determined and K_p or K_c is found to remain constant in all the experiments proving conclusively the reversibility of the reaction and the validity of the law of mass action.

It may be categorically stated that when the numbers of reactant and resultant molecules are equal in a reaction, its equilibrium constants (K_a and K_c) are equal and will be independent of pressure or volume. Similar results will be observed with the equilibrium of the following. Their equm. state will be unaltered with the variation of total pressure.

$$N_2+O_2 \rightleftharpoons 2NO\ ; \qquad CO+H_2O \rightleftharpoons CO_2+H_2\ ;$$
$$CO+NO_2 \rightleftharpoons NO+CO_2 \text{ etc.}$$

Example ; 2. The synthesis of ammonia.

$$N_2+3H_2 \rightleftharpoons 2NH_3$$

$$\begin{array}{llll} 1 & 3 & 0 & \text{....gr. moles initially present.} \\ 1-x & 3-3x & 2x & \text{....gr. moles present at equilibrium.} \end{array}$$

Suppose a (1 : 3) N_2—H_2 mixture attains equilibrium with NH_3 at a given temperature under a total pressure *P*. Let *x* moles out of 1 mole of nitrogen be transformed into ammonia, then the amount of ammonia formed would be $2x$ moles. At equilibrium, we have,

Components→	N_2	H_2	NH_3	Total
Initial amount	1	3	0	4 moles
Amounts at eqm.	$1-x$	$3-3x$	$2x$	$4-2x$ moles
Partial pressures	$\frac{(1-x)\,P}{4-2x}$	$\frac{(3-3x)\,P}{4-2x}$	$\frac{2x.P}{4-2x}$	P

$$\therefore\ K_p=\frac{p^2_{NH_3}}{p_{N_2}\times p^3_{H_2}}=\frac{(2xP/4-2x)^2}{\left[\frac{(1-x).P}{4-2x}\right]\left[\frac{(3-3x)\,P}{4-2x}\right]^3}$$
$$=\frac{4x^2\,(4-2x)^2}{27\,(1-x)^4.P^2}$$

If x is small compared to unity, the equation may then be written as $K_p = \frac{64x^2}{27P^2}$ or, $x^2 = \frac{27}{64}K_pP^2$,

When x, the fraction of the nitrogen converted into ammonia, is seen to be directly proportional.to the total pressure of P. That is, high pressure favours the formation of ammonia.

Example 3. Esterification of an acid.

The reaction between acetic acid and ethyl alcohol to form ethyl accetate (ester) is a familiar example of homogeneous equilibrium in liquid system.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

a	b	0	0	gr. moles present iaitially
$a-x$	$b-x$	x	x	gr. moles present at equilibrium.

Suppose 'a moles of acetic acid is mixed with 'b' moles of ethyl alcohol. Let at equilibrium x moles of ester is formed. Suppose the volume of the sysrem is v litres. Then the molar concentrations of the different components at equilibrium will be given by,

Components→	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
molar concentration at eqm :	$\frac{a-x}{v}$	$\frac{b-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

So, substituting in the mass law equation, we get

$$K_c = \frac{C_{ester} \times C_{H_2O}}{C_{acid} \times C_{alcohol}} = \frac{x/v \times x/v}{\frac{a-x}{v} \times \frac{b-x}{v}}$$

$$= \frac{x^2}{(a-x)(b-x)}.$$

Here, the volume is eliminated from the equation for equilibrium constant, and so the position of equilibrium is here independent of the total volume of the system. At eqm. the same quantity of ester will always be formed from a given quantity of acetic acid and alcohol. This reaction was investigated by Berthelot and St. Gilles who conclusively proved the validity of the law of mass action. In fact, as already stated, in any reaction in which the number of molecules does not change due to the reaction, the position of equilibrium is independent of the total volume of the system.

When alcohol and acid are mixed together in equimolecular proportion, it has been found that oniy 66·5 per cent of the acid is converted into ester at equilibrium. That is, for 1 mol, of acid and 1 mol. of alcohol, 0·665 moles are converted into ester and water. So, $a=1$, $b=1$, $x=0{\cdot}665$

$$\text{Hence } K_c=\frac{x^2}{(a-x)(b-x)}=\frac{(0{\cdot}665)^2}{(1-{\cdot}665)(1-{\cdot}665)}=4 \text{ (approx,).}$$

Knowing K_c, we can calculate the amount of ester formed for an initial concentration of substances involved in the reaction. Example : Calculate how much ester will be formed if 1 mole acetic acid is treated with 0·5 moles of alcohol.

Here $a=1$, $b={\cdot}5$ and since $K_c=4$; we have

$4=\frac{x^2}{(1-x)({\cdot}5-x)}$, whence $x=0{\cdot}423$ or $1{\cdot}57$, of which the latter value is inadmissible because 0·5 moles alcohol cannot produce 1·57 moles of ester. Hence, the number of moles of ester formed $=0{\cdot}423$' i.e. 42·3%.

15·7. **Le Chatelier's Principle :** When equilibrium is reached in a reversible reaction, the system has a definite pressure, temperature, concentration etc. The state of a chemical equilibrium is dependent on these factors. When any of these factors is altered, the position of equilibrinm is also altered. The way a system at equilibrium would behave, if any of these factors be changed, can be predicted by a universal principle, developed by Le Chatelier (1885). This is known as Le Chatelier's principle of mobile equilibrium which can be stated as follows :—

When a system at equilibrium is subjected to a stress caused by a change in any one of the factors controlling the equilibrium e.g., temperature, pressure, concentration etc. the system will tend to adjust itself in such a way as to relieve itself of that stress as far as possible.

That is systems in equilibrium react in such a manner as to minimise the effect of an external change imposed on the system.

This qualitative generalisation has been found to be applicable to all types of equilibrium, physical, chemical or mechanical.

We shall now discuss the effect of the change of various factors on chemical equilibrium in the light of Le Chatelier's principle.

1. *Effect of change in temperature,*— When heat is added to a system in equilibrium its temperature is raised. According to Le Chatelier's principle, under such a condition, the system will oppose the rise in temperature and will attempt to take away the applied heat. This eviddently is done if a change takes place in the system which occurs with absorption of heat (endothermic reaction). Similarly, if the temperature is lowered, the loss of heat will be compensated by causing more of exothermic process which evolves heat. In general, the principle predicts that *increase in temperature favours an endothermic change and decrease in temperature an exothermic change.* Accordingly the position of equilibrium is displaced with the change in temperature.

2. *Effect of change of pressure,*— If the pressure upon a system in equilibrium is increased, then according to the Le Chatelier's principle, the system will try to get rid of the additional pressure. This is achieved by the system if the reaction occurs in a direction in which there is a decrease in volume. So it can be stated that, *when the pressure of a system is increased the equilibrium is shifted in the direction in which the volume, and hence the number of molecules would diminish.*

For reactions, where the numbers of reactants and resultant molecules are equal, there is no volume change, the change of pressure will have no effect on the equilibrium position.

3. *Effect of addiiion of a component,*—If any of the components is added from outside at constant volume, its concentration increases and hence, according to the principle, the system tends to change in such a way as to decrease the concentration of

the added substance. This is done if the reaction in which the added component is used up is favoured. Thus, *the equilibrium point is displaced in that direction which minimizes the increase in the concentration of the added component.*

4. *Effect of Adding an inert gas*— If a non-reacting gas like argon or neon is introduced into the system at constant volume, (the pressure will of course change), the equilibrium constant and equilibrium point will not change because the partial pressures of of the reactants and the products remain unaffected. However if the inert gas be introduced at constant pressure, the total volume of the system will increase with consequent decrease of partial pressure of the components. Then the equilibrium will be displaced wherever K_p is dependent on pressure, though the equilibrium constant K_p will remain unchanged as K_p is independent of change of pressure. This can be easily ascertained by simple calculations in different cases.

From the foregoing considerations of Le Chatelier's principle it appears that,

(i) for exothermic reactions the yield is increased by lowering of temperature,

(ii) for endothermic reactions the yield is increased by increase of temperature,

(iii) in reactions entailing a contraction of volume, the yield is increased by increase of pressure.

(iv) in reactions resulting in an increase in volume, the yield is increased by lowering of pressure.

and (v) on addition at constant volume of any of the components of the left hand side of the equation, the reaction goes to the right and vice versa.

N. B. The position of equilibrium is shifted by a change of temperature or a change of pressure, but the underlying reasons are different. In the former case, the shift is due to a change in equilibrium constant itself. But in the latter case, the equilibrium constant is not affected, which has a constant value at a definite temperature. The equilibrium point changes with pressure because the mass law equation contains volume or pressure terms.

15-8. Application of Lc chateiier's principle in some technical reactions :

(a) Synthesis of Ammonia : Haber Process.

In the Haber Process, ammonia is synthesised in accordance with the following reaction, the amounts of nitrogen and hydrogen are kept in the molar ratio 1 : 3.

$$N_2+3H_2 \rightleftharpoons 2NH_3+23000 \text{ cals.}$$

(i) This is an exothermic reversible reaction, so high yield of ammonia will be obtained at lower temperature. At very low temperature, though the yield may be very high, the speed of reaction is very slow and so the time required to reach the equilibrium would be innconveniently long. Hence the reaction is carried out at an *optimum temperature* at which the speed of reaction is not too slow, nor the yield of ammonia is too low. The reaction is carried out in pressence of a catalyst to accelerate the reaction at the optimum temperature which depends on the catalyst used. For the above reaction using reduced iron as catalyst with molybdenum as promter, the optimum temperature is about 550°C.

(ii) The formation if ammonia takes place with a diminution in volume and hence the yield will be higher the greater the pressure. In practice, a total pressure of 200 atmospheres is applied in Haber's process, though pressures up to 1000 atmosphres have sometimes been employed. That the high pressure favours the formation of ammonia can also be predicted on the basis of Law of Mass Action.

If ammonia, formed at the high pressure and the optimum temperature, is removed immediately from the reaction vessel, the equilibrium position will change to produce more of ammonia.

(b) **Synthesis of Nitric oxide—** Nitric oxide is prepared by the combination of atmospheric nitrogen and oxygen. It is the main step in the manufacture of nitric acid by Birkeland and Eyde process.

$$N_2+O_2 \rightleftharpoons 2NO-44{,}000 \text{ calories.}$$

(i) The oxidation of nitrogen takes place with a large absorption of heat. The yield, therefore, will be increased by an increase in temperature. Actully nitrogen and oxygen are made to combine at a temperature of 3000°C in an electric arc when the conversion to NO is about 5% by volume. Not only high temperature but also efficient cooling of the products is essential. For, if the equilibrium mixture is cooled slowly, the percentage of nitric oxide will gradully decrease corresponding to lower conversion at these lower temperatures. To avoid this subsequent decomposition, the very hot equilibrium mixture is cooled down rapidly to temperatures lower then 1500°C, where the rate of decomposition is too slow to affect the composition of the mixture.

(ii) Since the number of molecules are equal on both sides of the equation, the yield of nitric oxide will be unaffected by a change of pressure.

(c) **Oxidation of Sulphur Dioxide :**

Sulphur trioxide is prepared by oxidising sulphur dioxide with aerial oxygen. This is the first step in the manufacture of sulphuric acid by contact proecss. The reaction is,

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45200 \text{ calories.}$$

(i) The reaction is strongly exothermic and reversible. So the yield of SO_3 is greater when the temperature is lower. But at low temperatures the rate of formation of SO_3 is very slow and so is not advantageous in an industrial operation. Hence, in the contact process, the reaction is conducted at an optimum temperature, at which the rate is not too slow, nor the yield is too low. A catalyst is used to accelerate the reaction at the optimum temperature. Finely divided platinum or vanadium pentoxide has been found to be the most suitable catalyst for the process, the optimum temperature being about 400°C to 450°C when about 99% conversion is obtained.

(ii) The formation of SO_3 takes place with a diminution in volume and hence the reaction has a possitility of higher yield at high pressure. But with the above working conditions the conversion $SO_2 \rightarrow SO_3$ is so complete that application of pressure makes no appreciable improvement of the yield. Hence the process is worked at ordinary pressure.

Ionic Equilibrium :

Weak acids and bases in solution remain partially dissociated into ions. These ions are in equilibrium with the undissociated molecules. All weak electrolytes show such ionic equilibria and the law of mass action is most aptly applicable in all such cases. For example :—

When acetic acid is dissolved in water, it dissociates as

$$\underset{1-\alpha}{CH_3COOH} \rightleftharpoons \underset{\alpha}{H^+} + \underset{\alpha}{CH_3COO^-}$$

Applying the law of mass action, the equilibrium constant, also known as the dissociation constant of the acid, can be expressed as follows :—

$$k_a = \frac{C_{H^+} \times C_{CH_3COO^-}}{C_{CH_3COOH}}$$

If 1 mole of acetic acid is present in *v* litres of the solution and α be its degree of dissociation, then the concentrations of unionised CH_3COOH, H^+ and CH_3COO^- at equilibrium are $\frac{1-\alpha}{v}$, $\frac{\alpha}{v}$ and $\frac{\alpha}{v}$ respectively. Therefore, by law of mass action, the dissociation constant K is given by

$K_a = \frac{\alpha/v \times \alpha/v}{(1-\alpha)/v} = \frac{\alpha^2}{(1-\alpha)v} = \frac{\alpha^2 c}{1-\alpha}$ where *c* is the concentration of the acid.

Similarly, in NH_4OH solution ; NH_4OH dissociates as

$$\underset{1-\alpha}{NH_4OH} \rightleftharpoons \underset{\alpha}{NH_4^+} + \underset{\alpha}{OH^-}$$

If 1 mole of NH_4OH is present in *v* litres of the solution and α be its degree of dissociation, then by law of mass action, the equilibrium constant also known as dissociation constant of the base, is given by

$$K_b = \frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_4OH}} = \frac{\frac{\alpha}{v} \times \frac{\alpha}{v}}{\frac{1-\alpha}{v}} = \frac{\alpha^2}{(1-\alpha)v} = \frac{\alpha^2 c}{1-\alpha}$$

where c is the concentration of the alkali.

At a given temperature, every weak acid and every weak base have fixed K_a and K_b values. The strength of a weak acid (or base) depends on the value of its dissociation constant. The higher the value of K_a, the greater is the strength of the weak acid.

The common ion effect on ionisation :— The ionisation of a weak electrolyte (a weak acid or a base) in solution is suppressed by the addition of a largely ionised salt having a common ion (present in the weak electrolyte). This is known as common ion effect. This can be understood in the following way :—

Let us consider the ionisation of acetic acid, $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$. If some sodium acetate be added to the acetic acid solution, the concentration of the common CH_3COO^- ion increases due to complete dissociation of sodium acetate as $CH_3COONa = Na^+ + CH_3COO^-$. Hence the equilibrium $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ shifts in the direction which reduces the concentration of CH_3COO^- ions (Le chatelier principle), i.e., the equilibrium shifts to the left forming some acetic acid. That is the extent of dissociation of acetic acid is decreased due to the addition of sodium acetate (having a common ion) with a consequent decrease in the concentration of H^+ ions.

Similarly, in the case of NH_4OH solution, aditiion of NH_4Cl, (which produces the common NH_4^+ ion on dissociation) will reduce the extent of ionisation of NH_4OH.

Thus the concentration of ions produced by the ionisation of weak electrolytes can be controlled by the addition of suitable electrolytes having common ion.

Hydrogen ion Concentration and pH Scale :—

Pure water is a very weak electrolyte and is slightly ionised : $H_2O \rightleftharpoons H^+ + OH^-$, the ionisation increases with rise of temperature.

At a given temperature, the dissociation constant of water is given by,

$$K_{H_2O} = \frac{C_{H^+} \times C_{OH^-}}{C_{H_2O}}.$$

$$\text{or,} \quad C_{H^+} \times C_{OH^-} = K_{H_2O} \times C_{H_2O}.$$

Since the dissociation is very small, the concentration of undissociated water, C_{H_2O}, may be regarded as constant, Hence,

$C_{H^+} \times C_{OH^-} = \text{constant} = K\omega$, where $K\omega$ is called *the ionic product of water.*

That is, in pure water or in dilute aqueous solutions, the product of the concentrations of H^+ ion and OH^- ion is constant, which is called the ionic product of water, K_w. At 25°C, K_w has the value 1×10^{-14}.

In pure water, the hydrogen and hydronyl ion cencentrations are equal, as each water molecule gives one H^+ and one OH^- ion on ionisation. Hence in pure water,

$C_{H^+} = C_{OH^-} = \sqrt{K_w} = 10^{-7}$ gram ions per litre at 25°C.

It is evident that in pure water or in an aqueous solution of a substance, both H^+ and OH^- ions must be present. Any one of the two cannot be totally absent, for, in that case, the ionic product of water (K_w) would be zero.

In a neutral solution, the H^+ and OH^- ion concentrations are equal, each being equal to 10^{-7} gram ions per litre.

In acid solution H^+ ion concentration exceeds the OH^- ion concentration, hence $C_{H^+} > 10^{-7}$ gram ion per litre.

In an alkaline solution, the OH^- ion concentration is greater than the H^+ concentration, hence $C_{H^+} < 10^{-7}$ gram-ion/litre.

Thus in a 0·001 (*M*) NaOH solution, the concentration of $OH^- = 1 \times 10^{-3}$ gm-ions/litre, assuming complete dissociation. Hence $C_{H^+} = K_w/C_{OH^-} = \frac{1 \times 10^{-14}}{1 \times 10^{-3}} = 1 \times 10^{-11}$ gm, ions/litre.

Similarly in a 0·01 (*M*) HCl solution, $C_{H^+} = 10^{-2}$ gm, ion/litre, hence $C_{OH^-} = K_w/C_{H^+} = \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = 1 \times 10^{-12}$ gm-ions/litre.

The H^+ ion concentrations are usually small and it is rather inconvenient to express them in terms of gm. ions per litre which involves figures with negative indices as 10^{-7} or 10^{-11} etc. Sorensen (1909) proposed a new scale, the *p*H scale, to express the H^+ ion concentration in aqueous solution. According to this system,

The negative logarithm to the base 10 of the hydrogen ion concentration is called the *p*H of the solution, i.e.,

$$pH = -\log_{10} C_{H^+}.$$

(i) In pure water, $C_{H_+} = 10^{-7}$, hence its $pH = -\log_{10} 10^{-7} = 7{\cdot}00$,

(ii) In 0·01 (*N*) HCl solution, $C_{H_+} = 10^{-2}$ (assuming complete dissociation)

$$\therefore \quad pH = -\log_{10} 10^{-2} = 2{\cdot}00,$$

(iii) In ·001 (N) NaOH solution.

$$C_{H^+} = \frac{K_w}{C_{OH^-}} = \frac{10^{-14}}{10^{-3}} = 10^{-11}. \quad \text{(assuming complete dissociation)}$$

$$\therefore \quad pH = -\log_{10} 10^{-11} = 11{\cdot}00 \text{ etc.}$$

So, it is obvious, that in neutral solution $pH = 7{\cdot}00$. In acid solution $pH < 7{\cdot}00$ and alkaline solutions have $pH > 7{\cdot}00$. The acidity and alkalinity of a solution can, thus, be conveniently expressed by a series of numbers between 0 and 14, as shown below.

C_{H^+}	$10^0(=1)$	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}
*p*H	0	1	2	3	4	5	6	7
C_{H^+}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}	
*p*H	8	9	10	11	12	13	14	

The greater the hydrogen ion concentration, the smaller is the *p*H of the solution.

Solubility product :—

When a sparingly soluble salt, say silver chloride, is shaken vigorously with water, a small amount of the salt will go into solution. The solution will be saturated with silver chloride and will be very dilute. AgCl in solution will remain completely dissociated into Ag^+ and Cl^- ions. An equilibrium is established between the solid AgCl and the ions in solution, as,

$$AgCl\,(s) \rightleftharpoons Ag^+ + Cl^-.$$

Applying the law of mass action to this equilibrium,

$$K = \frac{C_{Ag^+} \times C_{Cl^-}}{C_{AgCl(s)}}, \text{ where K is the equilibrium constant.}$$

Since, the active mass or concentration of solid is constant, we have,

$$C_{Ag^+} \times C_{Cl^-} = L \text{ (a constant).}$$

That is, the product of concentrations of the ions in saturated solution of the sparingly soluble salt AgCl is constant at a given temperature. This constant is called the solubility product of silver chloride, L_{AgCl}.

Similar phenomena are observed in case of other sparingly soluble salts. For example, with lead chloride,

$$PbCl_2(s) \rightleftharpoons Pb^{++} + 2Cl^- \ ; \ K = \frac{C_{Pb^{++}} \times C^2_{Cl^-}}{C_{PbCl_2(s)}}$$

$\therefore$ Solubility product, $L_{PbCl_2} = C_{Pb^{++}} \times C^2_{Cl^-}$

The solubility product of a sparingly soluble salt may then be defined as *the maximum product of the concentrations of its ions, raised to appropriate powers, in a saturated solution.* The solubility product of a sparingly soluble salt is constant at a given temperature.

Solubility and solubility product :—

The relation between the solubility and the solubility product of a sparingly soluble salt may be found out as follows. Let us consider silver chloride and let its solubility be S, expressed in gm-moles per litre. Since the salt dissociates completely in solution,

the concentration of $Ag^+ = S$ and the concentration of $Cl^- = S$.

∴ the solubility product, $L_{AgCl} = C_{Ag^+} \times C_{Cl^-}$

$$= S \times S = S^2.$$

i.e., the solubility product in this case is numerically equal to the square of the solubility of the salt. But the relation will be different in different cases. For example, in case of lead chloride,

$$PbCl_2 \rightleftharpoons Pb^{++} + 2Cl^-$$

If S be the solubility of $PbCl_2$ in gm-mols per litre, then

$C_{Pb^{++}} = S,\ C_{Cl^-} = 2S.$

∴ the solubility product $L_{PbCl_2} = C_{Pb^{++}} \times C^2_{Cl^-}$

$$= S \times (2S)^2 = 4S^3.$$

The solubility and solubilily products are thus correlated.

To a solution of a sparingly soluble salt, if a substance having an ion common with one of the ions of the salt be added, then the solubility of the salt is further reduced. This can be explained as follows.

When an amount of silver nitrate is added to a saturated solution of AgCl, the concentration of Ag^+ ions in solution increases. To maintain the constancy of L_{AgCl}, some ions have to be removed. As a result, some silver chloride is formed and being insoluble, it is thrown out as precipitate. Similarly, if some NaCl be added to AgCl solution (saturated), the concentration of Cl^- ions increases, But, to keep L_{AgCl} constant, some Cl^- ions will combine with Ag^+ ions to produce AgCl and are removed as precipitate. Hence the common ion (Cl^-) decreases the solubility of silver chloride.

Thus the solubility of a sparingly soluble salt is decreased by the presence of a common ion—but the solubility product remains constant.

Application of solubility product :—

(a) **Precipitation :** The solubility product is the maximum limiting value of the product of the concentrations of the two ions which can remain in solution. If the product of the concentrations of two ions in solution is made to exceed the value of solubility product, the law demands that ions are to be removed. As a result, the ions unite to form the sparingly soluble salt, which is thrown out of solution as a percipitate, i.e. when,

product of ions$>$solubility product, the substance precipitates.

This principle has been uitilised in qualitative analysis of different metals which are precipitated as their sparingly soluble salts. Some illustrations are given below.

(i) In Grup I, Ag^+, $Hg_2{}^{++}$ and Pb^{++} are precipitated by dilute HCl as their insoluble chlorides. The chlorides of these metals have low solubility product values. With the addition of HCl, sufficient Cl^- ions will be present and the product of the concentrations of metal ions and Cl^- ions will exceed the solubility product of these metallic chlorides. Hence they are precipitated.

(ii) In Group II, Cu^{++}, Hg^{++}, Cd^{++}, Bi^{+++} etc. are precipitated by H_2S as their sulphides in acid medium but the sulphides of Zn, Mn, Co. Ni etc. are not precipitated. This can be explained as fallows.—

H_2S is a very weak acid with a small dissociation $H_2S \rightleftharpoons 2H^+ + S^{--}$. The concentration of S^{--} ions in its saturated solution in water is small, which is further suppressed in acid solutions because of the presence of H^+ ions (common ion effect). Now suppose a solution contains Hg^{++}, Cu^{++}, Zn^{++}, Mn^{++} ions in acid medium and H_2S gas is passed through the solution. The concentration of sulphide ions is so much decreased due to the presence of H^+ ions that the product of concentration of metal ions and the sulphide ion can only exceed the solubility product of very insoluble sulphides (with low solubility product values) of group II metals, e.g., HgS, CuS, CdS, etc. and hence they are precipitated, whilst FeS, ZnS, MnS, etc. remain in solution as their solubility products are much higher. These sulphides will be precipated by passing H_2S gas in alkaline medium where the concentration of sulphide ions increases to a large extent so that the corresponding solubility product may be exceeded. In this way the precipitation of different metals as their sparingly soluble salts in qualitative analysis can be explained with the help of their solubility products.

(b) **Solubility of a precipitate :**

Let us consider a solid in contact with its saturated solution : $BA\ (solid) \rightleftharpoons B^+ + A^-$. If either B^+ or A^- ions are removed, the equilibrium gets disturbed and more BA dissolves to restore the the equilbrium. Therefore, any substance that removes B^+ or A^- ions helps the solution of BA.

AgCl which has very little solubility in water, readily dissolves in aqueous ammonia. To a saturated solution of AgCl (in contact with solid AgCl), when ammonia is added, silver ions form the complex $[Ag\,(NH_3)_2]^+$ ion. That is, simple Ag^+ ions are removed and consequently, the product of the concentrations of Ag^+ and Cl^- ions falls below the solubility product of AgCl. To maintain the constancy of solubility product of AgCl, solid silver chloride dissolves to provide the necessary Ag^+ ions. That is why silver chloride is found to be soluble in ammonia. For similar reasons cupric hydroxide dissolves in ammonia.

Magnesium hydroxide is sparingly soluble in water but dissolves readily in ammonium chloride solution. The following equilibrium in the saturated solution of magnesium hydroxide will be established, $Mg(OH)_2\ (solid) \rightleftharpoons Mg^{++} + 2OH^-$, and its solubility product $L_{Mg(OH)_2} = C_{Mg^{++}} \times C^2_{OH^-}$ is very low. On the addition of ammonium chloride ($NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$), the concentration of OH^- ion is reduced by combination with NH_4^+ ions to form weakly ionised NH_4OH and the equilibrium is thereby disturbed. As OH^- ions are removed from solution, Mg^{++} ions must increase to maintain the constancy of the solubility product, $L_{Mg\,(OH)_2}$. Hence more magnesium hydroxide goes into solution and the process continues until all the magnesium hydroxide is dissolved. For similar reasons $CaCO_3$, $Fe(OH)_3$, ZnS etc. are all dissolved in HCl.

Exercise—15

1. (a) What do you mean by reversible and irreversible reaction ? Give examples.

(b) What do you mean by the equilibrium state of a reversible reaction ? State the characteristics of a true equilibrium.

2. (a) "In a reversible reaction the state of equilibrium is dynamic in nature and never static"—justify this statement.

(b) Define equilibrium constant and obtain the relation between K_p and K_c.

3. (a) State the Law of mass action and explain the term active mass.

(b) Formulate the mass law expression for the reversible reactiou, $A + B \rightleftharpoons AB$. Hence derive the expressions for the eqilibrium constants for the reactions :—

(i) $H_2 + I_2 \rightleftharpoons 2HI$

(ii) $N_2O_4 \rightleftharpoons 2NO_2$

(iii) $2SO_2 + O_2 \rightleftharpoons 2SO_3$

(iv) $2H_2(l) + O_2(l) \rightleftharpoons 2H_2O(l)$

4. Discuss the influence of temperature and pressure on

(i) Equilibrium of a chemical system and

(ii) the equilibrium constant.

5. State Le chatelier's principle and explain how does it predict the effect of change of pressure and of temperature on the state of eqilibrium of the following reactions :—

(i) $N_2 + 3H_2 \rightleftharpoons 2NH_3 + 23{,}000$ cals.

(ii) $N_2 + O_2 \rightleftharpoons 2NO - 44{,}000$ cals.

(iii) $2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45{,}000$ cals.

6. (a) How the amounts of products in the reaction

$NO_2(g) + CO(s) \rightleftharpoons CO_2(g) + NO(g)$

would be influenced if the partial pressure of CO be raised by introducing CO from outside ?

(b) When 1 gm. mole of each of ethyl alchol and acetic acid are mixed, 0·667 gm-mole. of ethylacetate is formed at equilibrium. Find the equilibrium constant of the reaction

$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ [K=4,0]

7. A molar solution of a monobasic acid (HA) is 5% dissociated ; what is its dissociation constant K_a ? [$2{\cdot}5 \times 10^{-3}$]

8. (a) Define "solubility product". Give two examples to explain its significance. How does solubility product of a sparingly soluble salt relate to its solubility ?

   (b) Discuss, with illustrations, two important uses of solubility product.

9. (a) The solubility of Ag Br is $5{\cdot}75 \times 10^{-7}$ gm. mole per litre. What is its solubility product ?

   (b) The solubility product of PbF_2 is $3{\cdot}2 \times 10^{-8}$. How many milligrams of PbF_2 would be present per litre of its saturated solution ?

   [Pb = 207·2. F = 19] [(a) $3{\cdot}3 \times 10^{-13}$; (b) $4{\cdot}9 \times 10^{2}$mgs]

10. (a) Why will there be difference in the results if $CaCO_3$ is heated in the open and in a closed vessel ?

   (b) In the Haber process of ammonia production the following equ. is usesd :

   $$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 11{\cdot}8 \text{ KCal.}$$

   Will the reaction lead to completion if carried out in a closed vessel ? What will be the effect of continuous removal of ammonia produced.

PART II

(NON-METALS)

CHAPTER XVI

The Chemistry of Non-Metals.

The elements have been divided broadly into two classes, metals and non-metals. A study of the Periodic Table shows that the number of non-metallic elements is much smaller than the number of metals. But, so far as the distribution of the elements in nature is concerned, the non-metals like oxygen and silicon occur to a much greater extent than the metals. It is customary to study the chemistry of non-metals and their compounds first. Then we shall discuss the chemistry of metals and their compounds.

HYDROGEN

Atomic number 1. Atomic weight 1·0079, Molecular formula H_2, Electronic configuration 1s , Melting point—259°C, Boiling point —252·7°C, Density 1 litre weighs 0·089 gram at N.T.P.

16.1. History and occurrence : Hydrogen gas was first prepared by Robert Boyle in 1672. Later it was carefully studied by cavendish who showed it to be a constituent of water. For this reason, Lavoisier named it 'hydrogen' or 'water producer' in 1783.

In the free state, hydrogen occurs in small quantities in volcanic and other natural gases, in the outer atmosphere of the sun. In minute traces (about 1 part per million) it is found in air, because the speed of the hydrogen molecule at atmospheric temperature is sufficient for it to escape from the earth's gravitational field. But compounds of hydrogen are abundant in nature. In combination with oxygen, it is present in water. Almost all the organic compounds contain hydrogen, such as, oils, fats, proteins, carbohydrates, petrolium, wood, coal etc.

16 2. Preparation :—The chief sources of hydrogen are (1) acids, (2) alkalis and (3) water, as all these compounds contain hydrogen. Hence hydrogen may be prepared from these substances.

(1) **Hydrogen from acids** : Acids contain replaceable hydrogen atoms which can be displaced by metals which are placed above hydrogen in the electrochemical series, i.e. more electropositive than hydrogen. Thus hydrogen is easily liberated from dilute hydrochloric or sulphuric acid by the action of metals like zinc, magnesium and iron. Tin and aluminium react with hot and strong hydrochloric acid to produce hydrogen. Copper, silver, gold etc., which are less electropositive than hydrogen, cannot liberate hydrogen from the acids.

$Mg+H_2SO_4=MgSO_4+H_2$ $Sn+2HCl=SnCl_2+H_2$

$Fe+2HCl=FeCl_2+H_2$ $2Al+6HCl=2AlCl_3+3H_2$

Nitric acid, however, is not used for the preparation of hydrogen due to its strong oxidising property, which converts the liberated hydrogen into water. Only dilute nitric acid can produce hydrogen by the action of magnesium or manganese.

$$Mg+2HNO_3=Mg(NO_3)_2+H_2$$

Laboratory preparation : In the laboratory, hydrogen is most conveniently prepared by the action of moderately strong sulphuric acid (1 volume concentarted acid to 5 volumes of water) on granulated Zn.

Reaction : $Zn+H_2SO_4=ZnSO_4+H_2$

The reaction is slow if the zinc is pure so commercial zinc (impure) is used in the preparation of hydrogen. If pure zinc is used, a small quantity of cupric sulphate solution is added to the acid in order to deposit metallic copper on the surface of zinc, forming zinc-copper couple, which reacts readily with dilute acids.

Procedure : A quantity of granulated zinc (commercial) is taken in a two-necked Woulfe's bottle tightly fitted with corks. Through one cork passess a thistle funnel the end of which reaches nearly the bottom of the Woulfe's bottle and through the other passes a delivery tube whose outer end dips under water in a pneumatic trough (Fig 16·1). The apparatus is made perfectly air-tight, since hydrogen forms an explosive mixture with oxygen of air.

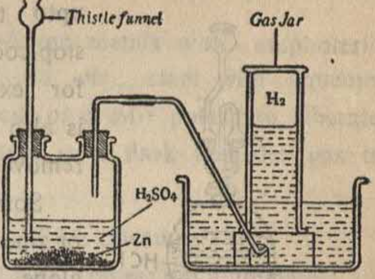


Fig 16·1. Preparation of hydrogen

Moderately strong H_2SO_4 (1:5) is then poured into the Woulfe's bottle down the thistle funnel. As soon as the acid comes in contact with zinc, a brisk reaction takes place with the evolution of hydrogen at the ordinary temperature. The gas is allowed to escape for some time in order to drive out the inside air completely. Then a gas jar filled with water is kept inverted over the end of the delivery tube under water in the trough. Hydrogen gas then collects in the jar by the downward displacement of water. The jar filled with hydrogen is then removed from the trough by closing the mouth of the jar, while still under water, with a glass plate and is kept with its mouth downwards. In this way several jars of hydrogen are collected and kept ready to study its properties. Hydrogen thus prepared is not pure.

Precautions : (1) The end of the thistle funnel must always dip under the acid-level inside the bottle. (ii) All the connections must be perfectly air-tight as hydrogen forms an explosive mixture with air. (iii) Before collecting the gas, air from inside the apparatus must be completely driven out. (iv) There should not be any naked flame nearabout.

Preparation of hydrogen in Kipp's Apparatus :

To get a ready and continuous supply of hydrogen whenever required, the gas is prepared conveniently in a Kipp's Apparatus (Fig 16.2).

The apparatus consists of two detatchable parts—(i) the lower part of two globes joined by a narow neck, the lowest globe is flattened at the bottom, (ii) the upper part is a single globe with a long tapering stem which fits air-tight to the mouth of the middle globe. The stem reaches almost upto the bottom of the lowest globe. A stop-cock is attached to the middle globe for exit of gases. The bottom globe is also provided with a glass stopper to remove the waste liquid.

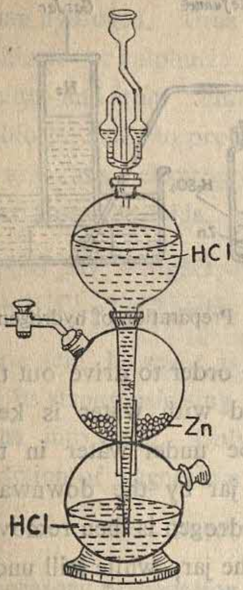


Fig. 16·2 Kipp's Apparateus

Some large pieces of granulated zinc or zinc sticks are placed in the middle globe. The stop-cock is then opened and moderately concentrated H_2SO_4 is poured in the upper most globe which runs down the long stem, fills up the lowest globe and comes up into the middle globe where it comes in contact with zinc. Chemical reaction immediately sets in, hydrogen gas is evolved which comes out through the stop.cock.

When the gas is not required the stop-cock is closed. The evolved gas cannot pass out and collects in the middle globe. This accumulated gas exerts pressure on the liquid level in the globe and forces down the acid into the bottom globe, some of which rises up the stem into the uppermost globe. As a result the contact between the acid and zinc breaks and consequently the evolutin of hydrogen ceases.

When the gas is required, the stop-cock is opened. The accumulated gas passes out, and so the pressure inside the middle globe falls. As a result the acid from upper globe comes down and enters into the middle, globe where coming in contact with zinc, it again produces hydrogen. The gas passes out through the stop-cock and is used as required.

The Kipp's Apparatus is always used for ready supply of a gas which is prepared by the action of a liquid upon a solid without application of heat, viz. for the preparation of carbondioxide hydrogen sulphide etc.

(2) **Hydrogen from alkalis** :—Some metals with amphoteric character like, aluminium, zinc, tin etc., reaet with aqueous solutions (20 to 30%) of caustic soda or caustic potash to liberate hydrogen. The reaction takes place in a flask and the gas is collected over water.

$Zn + 2NaOH = H_2 + Na_2ZnO_2$ (sodium zincate)

$2Al + 2KOH + 2H_2O = 3H_2 + 2KAlO_2$ (potassium aluminate)

$Sn + 2NaOH = H_2 + Na_2SnO_2$ (sodium stannite)

In the silicol process, hydrogen is prepared by the action of hot 20% caustic soda solution upon powdered silicon.

$Si + 2NaOH + H_2O = 2H_2 + Na_2SiO_3$ (sodium silicate)

(3) **Hydrogen from water** :—Water, being a common and important source of hydrogen, can produce the gas in different ways.

(a) **By the sction of metals upon water** :—Metals above hydrogen in the electrochemical series generally decompose water, giving off hydrogen, under different conditions which depend upon the nature of the metals.

(i) *Reaction wtth cold water* :—Some strongly electro-positive metals like sodium, potassium, calcium, barium etc. react vigorously with cold water and produce hydrogen at the ordinary temperature along with the hydroxide of the metals which dissolve in water.

$2Na + 2H_2O = 2NaOH + H_2$ $Ca + 2H_2O = Ca(OH)_2 + H_2$

$2K + 2H_2O = 2KOH + H_2$ $Ba + 2H_2O = Ba(OH)_2 + H_2$

Sometimes such reactions, particularly with sodium or potassium, occur so vigorously that the evolved hydrogen gets ignited in air as soon as it is liberated due to the generation of large amount of heat. To moderate such reactions, the metal is amalgamated with mercury and then added to water.

(ii) *Reaction with boiling water* :—When magnesium powder or aluminium powder or their amalgam or zinc-copper couple is boiled with water, hydrogen is evolved and the hydroxide of the metal is produced.

$$Mg + 2H_2O = Mg(OH)_2 + H_2$$
$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2$$
$$Zn + 2H_2O = Zn(OH)_2 + H_2$$

Mg and Al amalgams decompose also cold water slowly.

(*iii*) *Reaction with steam* :—Hydrogen is liberated when steam is passed over strongly heated metals like zinc, magnesium, iron, nickel etc. The oxides of metals are generally produced in these reactions, as the hydroxides are not stable at such high temperature.

$$Mg + H_2O = MgO + H_2$$
$$Zn + H_2O = ZnO + H_2$$
$$3Fe + 4H_2O = \underset{\text{(ferroso-ferric oxide)}}{Fe_3O_4} + 4H_2$$

Expt. :—Water is boiled in a flask and the issuing steam is passed through a porcelain or an iron tube loosely packed with iron filings and heated to redness in a furnace. Steam is decomposed by redhot iron and the evolved hydrogen, which comes out through the delivery tube, is collected over water in a gas jar. The laboratory arrangement is shown in Fig 16.3.

The metals which are below hydrogen in the electrochemical series have no action on water.

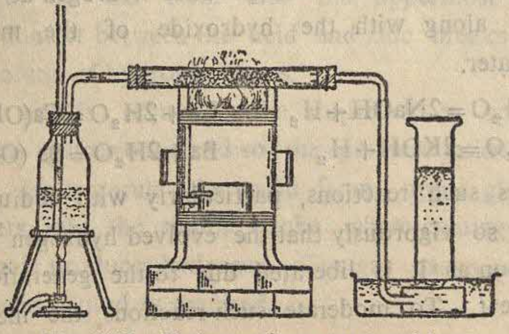


Fig. 16·3. Hydrogen from steam and iron

(**b**) **By the action of metallic hydrides upon water** :—Calcium hydride or hydrolith (CaH_2) and other salt-like ionic hydrides decompose water at the ordinary temperature and produce hydrogen.

$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$ $LiH + H_2O = LiOH + H_2$

(c) **By the action of carbon on water** :—When steam is passed over white-hot coke at 1000°C, a mixture of nearly equal volumes of carbonmonoxide and hydrogen, called water gas, is produced. At dull-red heat (i.e., at lower temperature) much carbondioxide is produced, its proportion decreases with rise of temperature.

$$C + H_2O = CO + H_2 \text{ (at bright red-heat)}$$
$$C + 2H_2O = CO_2 + 2H_2 \text{ (at dull red-heat)}$$

(d) **By the electrolysis of water** :—Hydrogen is obtained by the electrolysis of water. Since pure water is a poor conductor of electricity, it decomposes very slowly on passing current through it. But if the water is acidified wiith (say) sulphuric acid or made alkaline with baryta (barium hydroxide) or caustic soda, it is rapildiy electrolysed. Hydrogen is liberated at the cathode and oxygen at the anode, the added acid or alkali remains unaltered.

A laboratory arrangement for electrolysis of water is shown in Fig 16.4. The electrolysis is done in an apparatus called a voltameter. Two thin platinum foils are fused at the bottom of vessel which is half-filled with dilute sulphuric acid so that the platinum foils are kept immersed in the liquid. The ends of these platinum foils can be connected to the terminals of a battery and can serve as electrodes. Two graduated tubes, each with a stop cock at the upper end are fiilled up with the same dilute acid and are kept inverted over these pt-foils. Now electric current is passed through the acidulated water by connecting the two platinum foils with the two terminals of a battery. Water is decomposed giving off hydrogen and oxygen. Hydrogen is collected in tube over the cathode and oxygen in the tube over the anode. It is always found that the volume of oxygen liberated is nearly half the volume of hydrogen obtained. Best result is obtained by

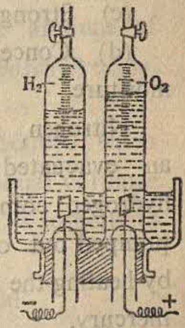


Fig. 16·4.
Electrolysis of water

electrolysing a dilute solution of barium hydroxide with nickel electrodes.

$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$ $Ba(OH)_2 \rightleftharpoons Ba^{++} + 2OH^-$

$H_2O \rightleftharpoons H^+ + OH^-$ $H_2O \rightleftharpoons H^+ + OH^-$

At the cathode : At the anode :

$H^+ + e = H$ $2OH^- = H_2O + O + 2e$

$H + H = H_2$ $O + O = O_2$

$$\therefore \; 2H_2O = 2H_2 + O_2$$

16.3 Preparation of Pure Hydrogen :—

(1) The hydrogen gas prepared from commercial zinc and dilute sulphuric acid in the Kipp's Apparatus is not pure. It is liable to contain as impurities, arsine (AsH_3), phosphine (PH_3), hydrogen sulphide (H_2S), sulphur dioxide, carbondioxide, possibly oxides of nitrogen, nitrogen and moisture. The gas is purified and dried by passing it, in succession, through a series of U-tubes containing the follwing :—

(a) lead nitrate solution to absorb H_2S,

(b) Silver sulphate solution to absorb AsH_3 and PH_3,

(c) Strong caustic potash solution to absorb SO_2, CO_2 and NO_2,

(d) Concentrated sulphuric acid or better P_2O_5 to absorb moisture.

Nitrogen, still present, may be removed by passing the gas in an evacuated bulb containing palladium foils which absorb hydrogen completely but not nitrogen. Unabsorbed nitrogen is pumped out of the bulb. Pure hydrogen is subsequently evolved by heating the bulb to dull-redness and the gas is collected over. mercury.

(ii) Very pure hydrogen is made by the electrolysis of warm solution of crystallised barium hydroxide in a glass U-tube, using nickel electrodes (Fig 16.5.). Water is decomposed liberating oxygen at the anode and hydrogen at the cathode. The hydrogen gas may be contaminated with small quantity of oxygen due to diffusion or leakage. So the gas is passed through heated platinum gauze taken in a bulb in order to convert the oxygen into water.

This moisture is then removed by passing the gas through bulbs

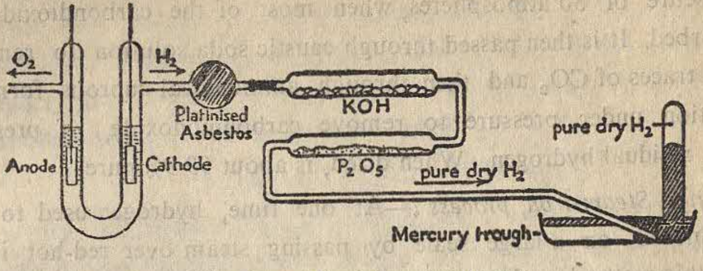


Fig. 16.5. Preparation of pure hydrogen

containing KOH and P_2O_5 in succession. The pure and dry gas is then callected over mercury.

16·4. Industrial Preparation of Hydrogen :—Large quantities of hydrogen are required in many industries, such as, the manufacture of ammonia, methyl alcohol, synthetic petrol, vanaspati etc. Zinc is too expensive a substance to be used in the manufacture of hydrogen. Large quantities of hydrogen are liberated as a by-product in the manufacture of caustic soda by the electrolysis of brine (See Vol II). The principal processes which are used for the manufacture of hydrogen are given below :—

(*i*) *Water gas process* :—Now-a-days, the largest amount of commercial hydrogen is obtained from water gas by *Bosch Process.* This process consists of three operations :—

(a) Steam is passed over white-hot coke at about 1000°C, when water gas is obtained, which is a mixture of nearly equal volumes of hydrogen and CO with a small amount as CO_2. It is sometimes used as a gaseous fuel.

$$C+H_2O=CO+H_2 \; ; \qquad \Delta H=+29000 \text{ cal}$$

(b) Since it is difficult to separate CO from H_2, water gas is mixed with excess of steam and the mixture is passed over a catalyst consisting of a mixture of ferric oxide and chromic oxide (promoter) heated to about 500°C. The following reaction occurs and more hydrogen is obtained.

$$(CO+H_2)+H_2O \rightleftharpoons CO_2+2H_2 \; ;$$

As the reaction is reversible, a little CO always remains in the gas.

(e) The resulting gas mixture is then led into water under a presseure of 30 atmospheres, when most of the carbondioxide is absorbed. It is then passed through caustic soda solution to remore last traces of CO_2 and then through ammoniacal cuprous formate solution under pressure to remove carbonmonoxide, if present. The residual hydrogen, When dried, is about 99 9% pure.

(*ii*) *Steam-iron process* :—At one time, hydrogen used to be produceed, on a large scale by passing steam over red-hot iron. But this method is almost obsolete now-a-days. In the *Lane* procees, spongy iron is heated to about 600°C – 800°C in vertical iron retorts, and steam is passed over it. The red-hot iron decomposes steam, liberating hydrogen and is itself converted to ferroso-ferric oxide, Fe_3O_4. : $3Fe+4H_2O \rightleftharpoons Fe_3O_4+4H_2$. The reaction is exothermic and reversible and the yield of hydrogen decreases with the rise of temperature. After the reaction Fe_3O_4 is reduced back to metallic iron by passing water gas through it, which is used over again.

$$Fe_3O_4+2(CO+H_2)=3Fe+2H_2O+2CO_2$$

The steaming and reduction processes are performed alternatively —the hydrogen obtained is 98% pure.

(*iii*) *Steam-Hydrocarbon Process* :—At present, hydrogen is very often produced in large quantities from different hydrocarbons found in natural gas or petrolium product by the action of steam.

(a) 'Natural gas' from petrolium wells contain mainly methane (CH_4) gas. This is mixed with steam and passed over a heated nickel catalyst at 700°C, when CO_2 and H_2 are obtained.

$$CH_4+2H_2O=CO_2+4H_2.$$

Hydrogen can also be produced from natural gas by its thermal decomposition (cracking). $CH_4=C+2H_2$.

(b) Propane gas (C_3H_8) produced in the distillation of petrolium also produces hydrogen, when it is mixed with steam and passed over heated (600°C) nickel catalyst. $C_3H_8+6H_2O=3CO_2+10H_2$

(c) Now-a-days, an important source of hydrogen is 'Naptha', which is obtained during the distillation of 'crude' of petrolium. The average composition of the hydrocarbon mixture present in 'naphtha' is C_7H_{15}. A mixture of naphtha and steam is passed over iron catalyst at 500°C, when a mixture of CO and H_2 is obtained. Carbonmonoxide is removed as in the Bosch process and hydrogen is obtained. In our country also the process is employed to produce ammonia in the fertiliser factories.

$$2C_7H_{15}+14H_2O=14CO+29H_2$$

(*iv*) *Electrolytic Process* :—Hydrogen is also obtained on a large scale by the electrolysis of a 20 per cent solution of sodium hydroxide in cells using iron cathodes and nickel plated anodes. The anodes and cathodes are placed alternately, the electrodes are separated from each other by porous asbestos diaphragm to prevent the hydrogen evolved at the cathode from mixing with oxygen liberated at the anode. Hydrogen evolved at the cathode of the different cells are collected together and is about 99·9% pure. The process is applicable for the manufacture of hydrogen only when the electricity is quite cheap.

16.5. Propertris of Hydrogen.

Physical Properties :—(i) Hydrogen is a colourless, tasteless and odourless gas. At extremely low temperature and under high pressure, it can be liquefied and finally solidified ; its b.pt.is − 252·7°C and m.pt. − 259°C. Neither liquid nor solid hydrogen possesses metallic properties.

(ii) Hydrogen is the lightest of all substances ; its density at N. T. P. is ·089 gm/litre. Air is 14·4 times heavier than hydrogen— that is why hydrogen filled balloons automatically rise up in the air.

Expt. : A gas jar filled with air is inverted over a jar filled with hydrogen and the cover glass of the latter jar is then removed. (Fig. 16·6). After few seconds, a lighted taper is introduced into the upper jar. It is found that the gas burns there with a slight explosion indicating that the upper jar now contains hydrogen gas, which, being lighter than air, has travelled to the upper jar displacing air from inside.

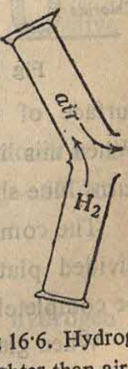


Fig 16·6. Hydrogen lighter than air

(iii) Hydrogen is almost insoluble in water. But it possesses the property of dissolving in certain metals like iron, cobalt, platinum and especially palladium forming solid solutions. This phenomenon is known as *occlusion* of hydrogen. Palladium occludes about 900 times its own volume of hydrogen at room temperature, which is released when the solid solution is heated. Use is made of this fact in the purification of hydrogen.

Chemical Properties :—(i) Hydrogen does not support combustion, but burns in air or oxygen with a pale blue non-luminous flame at the atmospheric pressure. Under great pressure, the flame becomes luminous. When a lighted splinter is introduced into a jar of hydrogen, the splinter is extinguished but the gas burns. A mixture of hydrogen with air or oxygen may be exploded on ignition.

(ii) Water is formed when hydrogen burns in air or oxygen. This reaction is exothermic and is used as a test for hydrogen :

$$2H_2+O_2=2H_2O\ ;\ \Delta H=-115{\cdot}6\ \text{Kcal}.$$

Expt. :—A stream of hydrogen, dried by passing through a U-tube containing fused $CaCl_2$, is burnt in a platinum jet. The gas continues to burn and the flame is allowed to impinge on the cold outer surface of a retort (Fig 16·7) through which cold water circulates. Drops of colourless liquid are formed on the cold outer surface of the retort and are collected inside a dish placed below. When this liquid is added to anhydrous copper sulphate, the latter turns blue showing that the liquid is water.

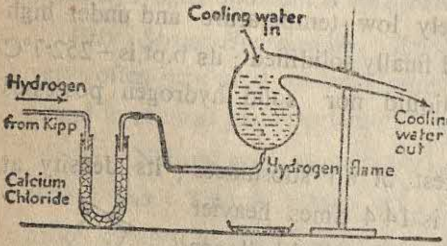


Fig 16·7. Hydrogen burns

The combination of hydrogen and oxygen is catalyst by finely-divided platinum. The reaction is, however, arrested if the gases be completely desiccated by prolonged exposure to P_2O_5.

When glass tubes of different widths and lengths are lowered over the flame of burning hydrogen, a musical note is produced and the flame begins to sing.

(iii) Hydrogen enters extensively into chemical combination with other elements—both metals and nonmetals. Its single valency electron in the K quantum shell is used in forming covalent or ionic links with other atoms. The type of bond it develops is decided by the electronegativity of the element with which it combines.

Reactions with metals :—Some strongly electropositive metals like alkali and alkaline-earth metals when heated in a current of hydrogen gas produce non-volatile salt like hydrides by establishing ionic bonds, e.g., LiH, NaH, CaH_2 etc. These hydrides are hydrolysed in contact with water.

$$2Li + H_2 = 2LiH \qquad LiH + H_2O = LiOH + H_2.$$
$$Ca + H_2 = CaH_2 \qquad CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$$

With feeble electropositive metals, hydrogen forms gaseous or volatille covalent hydrides, e.g., SnH_4, AsH_3, SbH_3 etc.

Reaction with non-metals :—In addition to oxygen, hydrogen combines with other non-metals also under suitable conditions establishing mostly covalent bonds. The covalent compound of hydrogen are volatile.

(a) *With halogens*, hydrogen combines readily. It reacts violently with fluorine even in the dark, but with chlorine, the reaction takes place in diffused sunlight· With bromine, the presence of bright sunlight is necessary. The reaction with iodine is somewhat slow and is reversible. In all cases the respective hydracids (HX) are produced.

$$H_2 + Cl_2 = 2HCl \qquad H_2 + I_2 \rightleftharpoons 2HI.$$

(*b*) *With nitrogen*, hydrogen combines to form ammonia at a high pressure (about 200 atmospheres) and temperature (~ 550°C) in presence of the catalyst iron.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

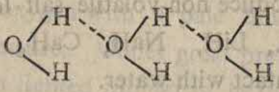
(*c*) *With Sulphur*, hydrogen combines to form hydrogen sulphide when the gas is bubbled through boiling sulphur,

$$H_2 + S = H_2S.$$

(*d*) *With Carbon.*—On striking an electric arc between carbon electrodes (2000°C) in an atmosphere of hydrogen, acetylene is produced. $2C+H_2=C_2H_2$.

An atom of hydrogen, previously bonded to one of the three elements nitrogen, oxygen and fluorine with high electronegativity, may link with another atom of one of these elements by a unique form of linkage known as the hydrogen bond. The hydrogen bond occurs in liquid water containing the molecule

$(H_2O)_3$ or



(iv) On account of its affinity for the electronegative elements oxygen and chlorine, hydrogen is frequently used as a reducing agent. If hydrogen is passed over the oxides of weakly electropositive metals, for example, CuO, HgO, Fe_2O_3, PbO etc. Water is formed, and the metal is set free.

$$CuO+H_2=Cu+H_2O\ ;\ PbO+H_2=Pb+H_2O$$

Oxides of strongly electropositive metals like sodium, potassium, calcium or magnesium, however, are hot reduced by hydrogen.

Expt. : A stream of hydrogen from a Kipp's Apparatus, dried by passing through a U-tube containing fused $CaCl_2$, is passed

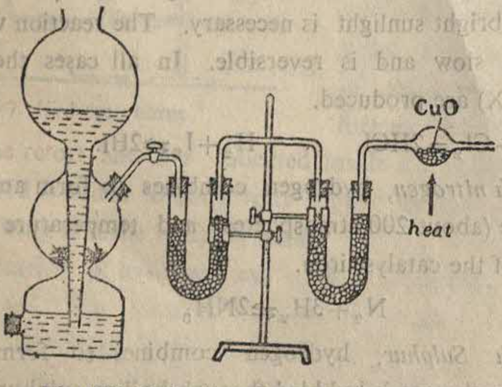


Fig 16·8 Reduction of CuO by hydrogen

over heated black copper oxide (CuO) taken in a bulb-tube

(Fig. 16.8). The black oxide is reduced to dull-red metallic copper and water is formed.

$$CuO + H_2 = Cu + H_2O.$$

In fact, this reducing property of hydrogen is utilised in extracting some metals from their oxides, as in the case of tungsten, molybdenum, etc.

$$WO_3 + 3H_2 = W + 3H_2O$$

(v) Uuder high pressure and temperature, hydrogen, reacts with carbon-monoxide in several different ways, the nature of the products depends on the catalyst used and also on the temperature and pressure employed. When a mixture of CO and H_2 is passed over a catalyst ($ZnO + Cr_2O_3$) at about 400°C, methyl alcohol is produced. It is of great commercial importance.

$$CO + 2H_2 = CH_3OH.$$

In the Fischer—Tropsch Process. (See Part II), a mixture of saturated and unsaturated hydrocarbons results.

(vi) Unsaturated organic compounds react with hydrogen in presenee of nickel catalyst at somewhat higher temperature and become saturated compounds.

$$\underset{\text{ethylene}}{H_2C = CH_2} + H_2 = \underset{\text{ethane}}{H_3C - CH_3}$$

This process is called *hydrogenation.* Uusaturated oils like groundnut oil, cotton seed oil etc. are thus treated with hydrogen gas in presence of nickel when saturated fats like "Vanaspati" are produced by hydrogenation.

16 6. Nascent Hydrogen :—Certain reactions can be brought about by systems of reagents generating hydrogen, although the some result cannot be obtained by the use of gaseous hydrogen previously prepared. For example, ferric chloride is reduced to ferrous chloride when a mixture of zinc and sulphuric acid is added to the solution. If, however, hydrogen gas is bubbled through a solution of ferric chloride, scarcely any reaction occurs. This peculiar activity of hydrogen in the former case is attributed to a special form of hydrogen which is termed as nascent (new-born) hydrogen, i.e., the hydrogen at the moment of its generation. Nascent hydrogen is more reactive and a more powerful reducing agent than ordinary hydrogen.

Expt. : (i) Into a portion of potassium permanganate solution acidified with dil. H_2SO_4, hydrogen gas is passed from a Kipp's Apparatus. No change in pink colour is observed. Now the remaining portion of acidified potassium permanganate solution is added to a mixture of zinc and dil. H_2SO_4. The pink colour of $KMnO_4$ gradually disappears indicating that potassium permanganate is reduced to manganous salt by nascent hydrogen.

$$2KMnO_4+3H_2SO_4+10H=K_2SO_4+2MnSO_4+8H_2O.$$

(ii) Sodium nitrate is dissolved in NaOH solution and hydrogen gas is passed into a portion of the solution. No smell of ammonia is given off. Now a piece of Al-foil is added to the remaining portion of the solution and is heated. $NaNO_3$ is reduced by nascent hydrogen and the smell of ammonia is obtained.

$$NaNO_3+H_2O+8H=NaOH+NH_3+3H_2O$$

Several views have been put forward to explain such enhanced activity of nascent hydrogen. namely ; (i) in the nascent state, hydrogen is present as atoms and is liberated under ligh pressure, hence this enhanced reactivity.

(ii) another view is that the nascent hydrogen is activated by the energy liberated in the reaction in which it is formed. This explains the fact that nascent hydrogen obtain from different sources are not equally reactive. Thus, a chlorate can be reduced to a chloride by the nascent hydrogen obtained from zinc and dil. H_2SO_4, but not by the nascent hydrogen obtained from Na-amalgam and water. Since in different reactions different amonnts of energy are liberated, the nascent hydrogen produced by different reaction is also energised to different extent—hence they possess unequal reactivity.

16.7. Atomic Hydrogen :—The molecule of hydrogen can be split up into two free hydrogen atoms according to the equation

$H_2 = H + H$; $\Delta H = +103$ Kcal. It absorbs large amount of heat. Atomic hydrogen is generally formed when hydrogen gas is forced through an electric arc between two tungsten rods, or when the gas under a very low pressure is subjected to electric discharge in a long tube. Once produced the atoms of hydrogen do not readily re-unite. Atomic hydrogen is very reactive. It combines directly with oxygen, phosphorus etc. at the ordinary temperature and reduces compounds of heavy metals, such as silver nitrate, mercuric chloride and cupric nitrate, to the respective metals.

When atomic hydrogen combines under suitable conditions to produce the molecular H_2, large amount of heat is expelled.

$$H + H = H_2 \text{ ; } \Delta H = -103 \text{ Kal.}$$

This can be used to obtain a very high tempreature of about 5000°C. This arrangement is often called a "hydrogen torch".

16 8. **Isotopes of hydrogen** :—Hydrogen has three isotopes. Its atomic masses are 1, 2 and 3. The isotopes are called hydrogen (H), deuterium or heavy hydrogen (D) and tritium (T). Hydrogen ${}^{1}_{1}H$; deuterium ${}^{2}_{1}H$; tritium ${}^{3}_{1}H$.

Of these, tritium is radioactive and hardly occur in nature. The relative abundance of the other two in nature are hydrogen 99 985%, deuterium 0·015%.

Deuterium resembles hydrogen in chemical properties which depends on electronic configuration, but it differs from hydrogen in physical properties like boiling point, latent heat of vaporisation etc. which are influenced by the mass of the nucleus.

16.9. Use of Hydrogen :—

(i) Hydrogen is required for large scale production of ammonia, methyl alcohol, hydrogen chloride, synthetic petrol etc.

(ii) It is essential for hydrogenation of oils to produce vanaspati-like fats.

(iii) The gas finds commercial application in oxyhydrogen blow-pipe for welding purposes.

(iv) It is used in balloons for its lightness, where helium is not available.

(v) It is used as a reducing agent in extracting some metals from their oxides.

(vi) Liquid hydrogen is one of the fuels for rockets.

Tests : (i) Hydrogen gas burns with a pale blue flame and forms drops of water. The water formed is tested with anhydrous white copper sulphate which turns blue.

(ii) Hydrogen is absorbed by spongy palladium which gives off the gas again on heating.

Exercise—16

1. Describe how you will proceed to prepare as pure a sample of hydogen as possible, in the laboratory. What precautions should be taken in collecting the gas ?

2. Under what conditions do oxygen and hydrogen combine to form water ? How would you show (a) that water is formed when hydrogen is burnt in air, and (b) that hydrogen is a reducing agent ?

3. How is a continuous supply of hydrogen obtained in the laboratory ? Give a neat sketch of the apparatus used. Explain the function of the apparatus and state the advantanges of its use.

4. (a) By what metals and under what conditions is water decomposed with liberation of hydrogen ?

(b) What is nascent hydrogen ? How would you prove that it is more active than ordinary hydrogen ?

5. State the conditions under which hydrogen reacts with (i) copper oxide, (ii) chlorine, (iii) nitrogen, (iv) oxygen, (v) calcium and (vi) carbon monoxide. Give equations.

6. How is hydrogen produced on a manufacturing scale ? Mention the important uses of hydrogen.

7. Write explanatory notes on :—

(i) occlusion , (ii) oxy-hydrogen flame , (iii) isotopes of hydrogen , (iv) hydrogenation, (v) hydrolith process.

8. Explain why—

(i) commercial zine, but not not pure zine is used for the preparation of hydrogen,

(ii) dilute H_2SO_4, but not conc. H_2SO_4 is used in the preparation of hydrogen.

(iii) hydrogen gas when poured out flow upwards.

(iv) hydrogen is liberated at the anode when fused metallic hybride is electrolysed but it is liberated at the cathode when water is electrolysed,

CHAPTER XVII

OXYGEN

Atomic No. 8. Atomic wt 16 by definition, Mol. formula O_2, Electronic configuration $Is^2 2s^2 2p^6$, Melting point—218·4°C, Boiling point—183°C, Density 1 litre at N.T.P. weighs 1·429 gm.

17.1. History and occurrance :—Oxygen was discovered by Scheele and Priestley independently in 1774. But it was Lavoisier who proved the presence of oxygen in air and recognised its importance in combustion and respiration.

Oxygen is the most abundant of all the elements in the earth's crust, forming nearly fifty per cent of it. It is present in the free state in the atmosphere of which it forms about 21% by volume. Combined with other elements it occurs in water, sand, most of the rocks and minerals, and in many organic substances in the plant and animal kingdom.

17.2. Preparation :—Oxygen may be preparaed (i) by thermal decomposition of many oxygen-rich compounds, (ii) by decomposition of some metallic oxides at high temperature, (iii) by the electrolysis of water and (iv) from air.

(*i*) *From oxygen-rich compounds :*—

Compounds containing a large proportions of oxygen generally decompose at higher tempratures to give off oxygen. Thus oxygen is liberated by strongly heating certain oxy-salts (like chlorate, bromate, nitrate, permanganate, dichromate etc.) and oxyacids (such a sulphuric and nitric acids) containing anions rich in oxygen.

(a) The nitrates of alkali metals yield corresponding nitrites and oxygen, while nitrates of heavy metals give off oxygen along with the metallic oxide and oxides of nitrogen.

$$2KNO_3 = 2KNO_2 + O_2 \qquad 2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

(b) Chlorates, bromates and iodates particularly of the alkali metals, give the corresponding halides and oxygen.

$$2KClO_3 = 2KCl + 3O_2$$

(c) Potassium permanganate $KMnO_4$ and potassium dichromate $K_2Cr_2O_7$ decompose on heating giving off oxygen.

$2KMnO_4 = K_2MnO_4$ (potassium manganate) $+ MnO_2 + O_2$

$4K_2Cr_2O_7 = 4K_2CrO_4$ (potassium chromate) $+ 2Cr_2O_3 + 3O_2$.

Labarotory Preparation : In the laboratory oxygen is always prepared from potassium chlorate. When pure potassium chlorate is heated, it melts at about 360°C and is slowly transformed into potassium perchlorate $KClO_4$ and chloride, the mass becomes pasty. On further heating at about 630°C, the perchlorate decomposes to give off oxygen.

$$4KClO_3 = 3KClO_4 + KCl$$
$$KClO_4 = KCl + 2O_2$$

If however a little MnO_2 is added, $KClO_3$ decomposes at a much lower temperature (240°C) with rapid evolution of oxygen. MnO_2 acts as a catalyst and remains unchanged chemically.

Procedure : Five parts of $KClO_3$ and one part of powdered MnO_2 are mixed thoroughly and taken in a hard glass test-tube. The test-tube is fitted with a cork carrying a delivery tube, the further end of which dips under water in a pnumatic trough and a gas jar filled with water is kept over it. The hard glass test-tube is clamped in a horizontal but slightly inclined position as in Fig 17·1, in order to leave a passage over the mixture for the escape of oxygen. The test-tube is then heated carefully when the reaction starts and oxygen is given off. The source of heat is removed whenever the evolution of the gas becomes very rapid. The evolved oxygen passes out through the delivery tube and is collected in the gas jar by the downward displacement of water.

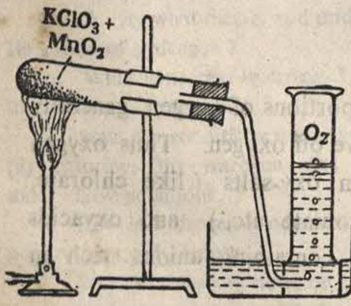


Fig. 17·1. Preparation of oxygen

$$2KClO_3 = 2KCl + 3O_2.$$

The manganese dioxide can be recovered unchanged in mass and composition from the residue left in the test-tube after the reaction by boiling with water, when KCl and unreacted $KClO_3$ dissolve leaving behind MnO_2 which is separated by filtration. The black residue of MnO_2 is then washed, dried and weighed—the weight will be found to the same as taken originally in the mixture. This MnO_2, which has been recovered, may be used over again in the reaction Thus MnO_2 simply acts as a catalyst, it only accelerates the decomposition of potassium chlorate.

Warning :—MnO_2, if contaminated with combustible impurities such as charcoal or antimony sulphide, explodes violently when heated with $KClO_3$ causing fatal accidents. Hence a little of the mixture should be separately heated before starting the experiment to make sure that no explosion occurs.

N.B. In addition to MnO_2, some other substances like platinum black, oxides of copper, iron, cobalt, nickel etc. facilitate the evolution of oxygen from $KClO_3$.

(d) Concentrated nitric acid or concentrated sulphuric acid, when allowed to fall drop by drop on red-hot pumic stone, give off oxygen by decomposition as follows :—

$$4HNO_2 = 4NO_2 + 2H_2O + O_2$$
$$2H_2SO_4 = 2SO_2 + 2H_2O + O_2$$

Expt. :—Some pumic stones are taken in a distilling flask fitted with a dropping funnel and a delivery tube (Fig 17.2). The flask is heated strongly and concentrated HNO_3 is allowed to fall drop by drop on red hot pumic stone from the funnel. The evolved gas is allowed to pass through a U-tube cooled in a freezing mixture, in which nitrogen dioxide condenses to a liquid and oxygen passes out, which is collected over water.

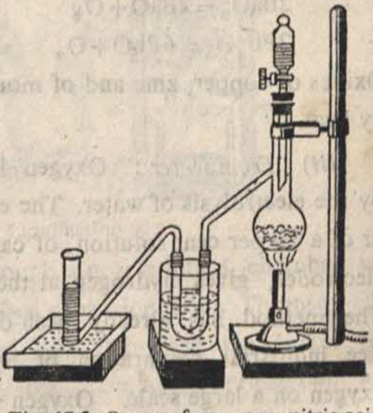


Fig. 17·2. Oxygen from conc, nitric acid

(e) Sometimes, for instant supply of oxygen in limited quantities, oxygen is obtained by the action of water on sodium peroxide.

Expt. :—Some dry sodium peroxide is taken in a conical flask fitted with a rubber stopper through which passes a dropping funnel containning water and also a delivery tube (Fig 17.3). Water is then added drop by drop to sodium peroxide. A rapid stream of oxygen is evolved without the application of heat. The evolved gas is as usual collected by displacement of water.

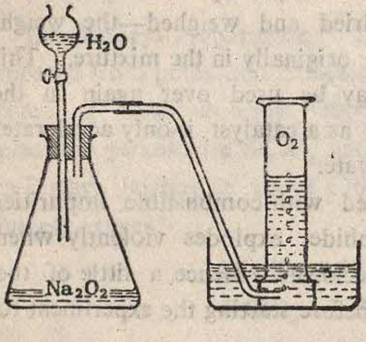


Fig 17·3. Oxygen from sodium peroxide

$$2Na_2O_2+2H_2O=4NaOH+O_2$$

(*ii*) *From metallic oxides* :

Oxides of feebly electropositive metals, such as, silver oxide and mercuric oxide, and most higher oxides and peroxides, such as BaO_2, PbO_2, CrO_3 etc, part with their oxygen wholly or partially when strongly heated.

$$2Ag_2O=4Ag+O_2 \qquad 2HgO=2Hg+O_2$$

$$2BaO_2=2BaO+O_2 \qquad 2PbO_2=2PbO+O_2$$

$$2Pb_3O_4=6PbO+O_2 \qquad 4CrO_3=2Cr_2O_3+3O_2$$

Oxides of copper, zinc and of more basic metals are not decomposed by heat.

(*iii*) *From water* : Oxygen is obtained together with hydrogen by the electrolysis of water. The electrolysis of dilute baryta solution or of a 20 per cent solution of caustic soda, using iron or nickel electrodes, gives hydrogen at the cathode and oxygen at the anode. The method has already been discussed in the previous chapter (see industrial preparation of hydrogen) and is used to produce oxygen on a large scale. Oxygen so prepared is liable to contain traces of ozone and hydrogen. Oxygen is stored and transported in steel cylinders at pressure of 100 atmospheres or so.

(*iv*) *From air* :—**Manufacture of Oxygen** :

(a) Previously, large amount of oxygen for industrial purposes used to be obtained from air by Brin's process. When BaO is heated in contact with air to dull red heat (500°C), it absorbs oxygen from air producing BaO_2, which subsequently gives off oxygen, when heated in vacuum to a higher temperature and reconverted into BaO.

$$2BaO + O_2 = 2BaO_2 \qquad 2BaO_2 = 2BaO + O_2$$

The process, which is an indirect method of obtaining oxygen from air, is now completely obsolete.

(b) Now-a-days oxygen is prepared on a large scale by the fractional distillation of liquid air.

Air contains about 21% oxygen by volume. The air is first freed from CO_2 and dried. Then it is highly compressed to about 200 atmospheres and cooled by running water. The cooled compressed gas is then pumped down a jacketted spiral tube (Fig 17.4) and allowed to expand suddenly through a nozzle into a chamber where the temperature falls due to free expansion (Joule-Thomson effect). The cold air is now allowed to circulate through the jacket round the spiral tube, thereby cooling the incoming compressed air, which again on sudden expansion cools down further. The process is repeated till finally air liquefies on expansion. Liquid air is mainly

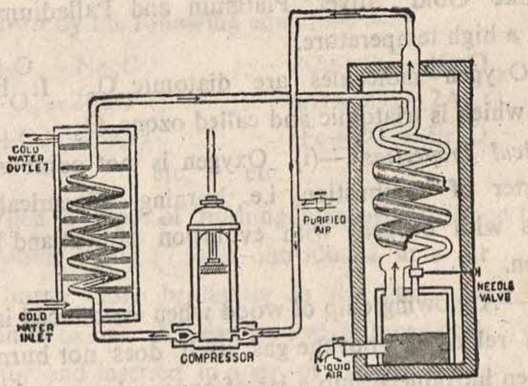


Fig. 17·4. Liquifaction of air

a mixture of liquid oxygen (b.pt.—183°C) and liquid nitrogen (b.pt.—196°C). The liquid air is then subjected to fractional distillation using a tall fractionating column, when more volatile nitrogen escapes leaving behind oxygen. Repeated cycles of the process give almost pure liquid oxygen. Finally, the liquid oxygen is evaporated and the compressed gas is stored in a steel cylinder under pressure.

17 3. Properties of Oxygen :—

Physical Properties :—(i) Oxygen is a colourless, odourless gas. It supports respiration and is essential to the life of animals and plants. It is a little heavier then air. At very low temperature and under high pressure it can be condensed to a pale blue liquid, which freezes to a blue solid if cooled in a tube immersed in liquid hydrogen. Liquid and solid oxygen are strongly magnetic.

(ii) Oxygen is slightly soluble in water, only obout 3 percent by volume at 0°C. But this small quantity of dissolved oxygen in water is of immense importance to aquatic life for their respiration. Metals like Gold, Silver, Platinum and Palladium can absorb oxygen at a high temperature.

(iii) Oxygen molecules are diatomic, O_2. It has also an allotrope which is triatomic and called ozone, O_3.

Chemical Properties :—(i) Oxygen is not combustible but it is a supporter of combustion, i.e., burning. Chemical reaction of substances with oxygen, with evolution of heat and light is called combustion.

Expt :—A glowing chip of wood when introduced into a jar of oxygen is rekindled, but the gas itself does not burn. A lighted candle when introduced into a jar of oxygen burns with a brighter flame.

(ii) Oxygen is chemically very reactive. It directly combines with many elements (both metals and nonmetals) and compounds, slowly at room temperatures and vigoursly with the evolution of heat and light it the temperature is raised. In some reactions. however, heat is absorbed.

The expected structure of the diatomic oxygen molecule would be $O=O$ or $:\ddot{\underset{..}{O}}:\,:\ddot{\underset{..}{O}}:$.

The oxygen molecule, normally possesses the structure $:\ddot{O}:\,:\ddot{O}:$; in which one pair of electrons is shared leaving two unshared electrons, one in each atom. The presence of unshared electrons is responsible for the paramagnetic behaviour of oxygen molecule and its large heat of dissociation (118·2 K cals per mole). In various compounds oxygen atom exerts ionic (eg. in CaO), covalent (e.g. in H_2O) or co-ionic bonds e. g. in $POCl_3$).

(*a*) *Combination of Oxygen with metals* :—

Many metals burn in oxygen when heated and produce metallic oxides which are mainly basic oxides, the reactions being exothermic. Alkali metals (Na, K, etc.) however, form their oxides at ordinary temperature. Some oxides like Al_2O_3, ZnO, PbO etc. are amphoteric. During burning, some metals produce flames of characteristic colours (sodium—*golden yellow*, potassium—*lilac or violet*, calcium—*brick red* etc.) The combination of metals with oxygen are shown by the following equations :—

$2Na+O_2=Na_2O_2$ $\qquad$ $2Cu+O_2=2CuO$

$2Ca+O_2=2CaO$ $\qquad$ $4Al+3O_2=2Al_2O_3$

$2Mg+O_2=2MgO$ $\qquad$ $3Fe+2O_2=Fe_3O_4$

etc. etc.

Expt :—When a piece of burning magnesium ribbon taken in a deflagrating spoon, (Fig 17.5) is introduced in a jar of oxygen it burns more brilliantly in the gas, producing magnesium oxide. A clean iron wire tipped with burning sulphur and inserted in a jar of oxygen burns vigourously, throwing off white-hot particles of molten ferroso-ferric oxide.

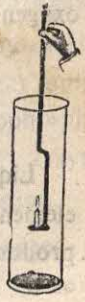


Fig. 17·5.
Deflagrating spoon

(*b*) *Combination of Oxygen with Non-Metals* :—

The non-metals like hydrogen, Carbon, Sulphur, phosphorus ; etc. burn in oxygen and their oxides are formed, which are acidic oxides. Nitrogen combines with oxygen at a very high temperature to produce nitric oxide, the reaction is highly endothermic. The combination of non-metals with oxygen are shown by the following equations :—

$C+O_2=CO_2$ $P_4+5O_2=2P_2O_5$

$2H_2+O_2=2H_2O$ $N_2+O_2=2NO$ (at 3000°C)

$S+O_2=SO_2$ etc. etc.

Expt :—A piece of burning phosphorus taken on a deflagrating spoon is introduced into a jar of oxygen, when phosphorus burns with a dazzling white light forming dense white cloud of phosphorus pentoxide. When shaken with water, the product of combustion produce phophoric acid, which turns blue litmus red.

$P_4+5O_2=2P_2O_5$ $2P_2O_5+6H_2O=4H_3PO_4$.

A few noble metals like platinum and the halogens are not directly attacked by oxygen.

The reactions involving the addition of oxygen to a substance or the removal of hydrogen from a substance are called '*oxidation*' reactions. The combination of oxygen with metals and non-metals are therefore instances of oxidation ; oxygen is the oxidising agent.

(*c*) *Reaction with Compouuds* :—Many Compounds are also oxidised by oxygen. Oxygen react with compounds of elements which themselves combine with oxygen, For example :

Gases such as methane, CH_4 and hydrogen sulphide, H_2S, burn in excess of oxygen, forming the oxides of the elements. Carbon monoxide, CO, is oxidised to CO_2 when heated in presence of oxygen.

$$CH_4+2O_2=CO_2+2H_2O$$
$$2H_2S+3O_2=2H_2O+2SO_2$$
$$2CO+O_2=2CO_2$$

Liquids and solids which are composed largley or entirely of elements which combine with oxygen will burn in oxygen and produce a mixture of oxides of the constituent elements. Thus—

C_2H_5OH (ethyl alcoho)$+3O_2=2CO_2+3H_2O$

CS_2 (Carbondi sulphide)$+3O_2=CO_2+2SO_2$

2PbS (lead sulphide)$+3O_2=2PbO+2SO_2$

2ZnS (zinc sulphide)$+3O_2=2ZnO+ SO_2$

Some compounds which are not easily oxidised by oxygen under ordinary conditions, can be oxidised in presence of a suitable catalyst. Thus,—

$$2SO_2+O_2 \xrightarrow[450°C]{Pt\ or\ V_2O_5} 2SO_3$$

$$4NH_3+5O_2 \xrightarrow[750°C]{Pt\ gauze} 4NO+6H_2O$$

Colourless nitric oxide, NO is, however oxidised to brown, nitrogen dioxide, NO_2 by simply bringing it in contact with oxygen —the reaction is used as a test for oxygen.

$$2NO+O_2=2NO_2$$

The rusting of iron is also an oxidation of iron to hydrated ferric oxide in presence of moisture.

Solutions of many—ous salts are oxidised to —ic salts in cold in suitable media ; e.g.

$$4\ FeSO_4+2H_2SO_4+O_2=2Fe_2(SO_4)_3+2H_2O$$
$$2\ SnCl_2+4HCl+O_2=2SnCl_4+2H_2O$$
$$2\ Cu_2Cl_2+4HCl+O_2=4CuCl_2+2H_2O$$

Sulphurous acid is also oxsidised by oxygen. to sulphuric acid.

$$2H_2SO_3+O_2=2H_2SO_4$$

(iii) In respiration, oxygen, performs the oxidation of sugars etc. in the living cells and return CO_2 to the atmosphere. Life is thus sustained by oxygen.

$$C_6H_{12}O_6\ (glucose)+6O_2 \rightarrow 6CO_2+6H_2O\ ;\ \Delta H=-673\ Kcals.$$

(iv) Oxygen is readily absorbed by (a) alkaline pyrogallate solution, (b) acidified solution of chromous chloride, (c) ammoniacal cuprous chloride solution, (d) sodium hypophosphite solution. In such absorption, chemical changes occur. Oxygen can be removed from a mixture by using one of these solution.

17.4. Isotopes of oxygen :—Three isotopes of oxygen are found having atomic masses of 16, 17, and 18 amu. These are ${}^{16}_{8}O$, ${}^{17}_{8}O$, ${}^{18}_{8}O$. The proportion of their abundance in nature is

$${}^{16}O : {}^{17}O : {}^{18}O = 99{\cdot}76 : 0{\cdot}04 : 0{\cdot}20$$

17.5. Uses of oxygen :—We are so accustomed to make use of the oxygen of the air that we often forget its importance. The uses of oxygen are as follows.

(i) The most important use of oxygen is in the process of respiration on which depends the entire living kingdom. The pure gas is often fed to patients suffering from breathing difficulties as in pneumonia.

(ii) The combustion of all fuels like coal, wood, oil etc. require oxygen.

(iii) In submarines, in mines, tunnels, mountaineering etc. oxygen cylinders have to be supplied as aids to respiration.

(iv) It is requird in the manufrcture of sulphuric and nitric acids and in steel industry.

(v) For producing high temperatures suitable for welding and cutting metals, oxy-hydrogen or oxy-acetylene flames are often used.

These flames are produced in specially designed blow pipe which consist of two coaxial tubes ending in jets (Fig 17·6.). Through the inner tube pure oxygen gas is passed and through the outer tube, hydrogen or acetylene gas, as the case may be, is passed and is ignited at the jet. The gas burns brilliantly in the continuous current of oxygen and the hot pointed flame attains a high temperature of about 2800°C in case of oxy-hydrogen flame and 3200°C in case of oxy-acetylene flame.

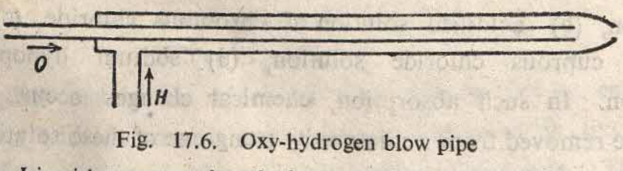


Fig. 17.6. Oxy-hydrogen blow pipe

(iv) Liquid oxygen, in admixture with carbonaceous materials like charcoal, has been used as an explosive.

17·6. : *Tests* : (i) A glowing chip of wood when introduced in a jar of oxygen is rekindled.

(ii) Oxygen forms reddish-brown fumes of nitrogen dioxide when brought in contact with nitric oxide,

(iii) It is absorbed by (a) alkaline pyrogallate solution producing a brown solution and (b) ammoniacal cuprous chloride solution giving a deep-blue solution.

OXIDES

17.7. Oxides are binary compounds formed between oxygen and any other element—metallic or nonmetallic. Almost all the elements (with the exception of inert gases) from oxides under suitable conditions. These oxides as already stated, may be covalent or electrovalent compounds. The oxides may be classified into the following different groups on the basis of their characteristie properties.

(1) **Acidic oxides :** An acidic oxide is an oxide which reacts directly with a base to form salt or with an alkali to form a salt and water. For example, carbon dioxide is an acidic oxide as it reacts with the base, calcium oxide, to yield the salt, calcium carbonate.

$$\underset{\text{(acidic oxide)}}{CO_2} + \underset{\text{(base)}}{CaO} = \underset{\text{(salt)}}{CaCO_3}$$

Similarly sulphur dioxide reacts with the alkali, sodium hydroxide, yielding sodium sulphite (salt) and water. Hence sulphur dioxide is also an acidic oxide.

$$\underset{\text{(acidic oxide)}}{SO_2} + \underset{\text{(alkali)}}{2NaOH} = \underset{\text{(salt)}}{Na_2SO_3} + \underset{\text{(water)}}{H_2O.}$$

Generally the acidic oxides are the oxides of non-metallic elements, such as CO_2, SO_2, SO_3, P_2O_5, N_2O_5 etc.

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O$$

$$P_2O_5 + 6KOH = 2K_3PO_4 + 3H_2O$$

$$SO_3 + Na_2O = Na_2SO_4$$

An acidic oxide, if soluble, combines with water to yield an acid, and hence it is called an acid anhydride, e.g., CO_2 (carbonic anhydride), P_2O_5 (phosphoric anhydride), SO_3 (sulphuric anhydride), N_2O_5 (nitric anhydride) etc.

$CO_2 + H_2O = H_2CO_3$ (carbonic acid)
$P_2O_5 + 3H_2O = 2H_3PO_4$ (phosphoric acid)
$SO_3 + H_2O = H_2SO_4$ (sulphuric acid)
$N_2O_5 + H_2O = 2HNO_3$ (nitric acid).

The higher oxides of some metals (e.g., CrO_3, Mn_2O_7 etc.) are also acidic and forms salts and water with alkalis. For example,

$CrO_3 + 2KOH = K_2CrO_4$ (potassium chromate) $+ H_2O$
$Mn_2O_7 + 2KOH = 2KMnO_4$ (potassium permanganate) $+ H_2O$

Certain oxides, such as stannic oxide, SnO_2 and silicon dioxide, SiO_2, which are insoluble in water, react similarly with fussed sodium hydroxide,

$$SnO_2 + 2NaOH = \underset{\text{(sodium stannate)}}{Na_2SnO_3} + H_2O$$

and are therefore classed as acidic oxides.

(ii) **Basic oxides :** A basic oxide is one which reacts with an acid to produce salt and water only.

$\underset{\text{(basic oxide)}}{CaO} + 2HCl = CaCl_2 + H_2O$; $\underset{\text{(basic oxide)}}{MgO} + H_2SO_4 = MgSO_4 + H_2O$

Basic oxides are generally the oxides of metals, in which the oxygen atoms and the metallic atoms are ionically linked, e.g., CuO, MgO CaO, Na_2O, FeO, ZnO etc.

basic oxides acids salts water basic oxides acids salts water
$ZnO + 2HCl = ZnCl_2 + H_2O$ $CuO + H_2SO_4 = CuSO_4 + H_2O$
$FeO + 2HCl = FeCl_2 + H_2O$ $Na_2O + 2HCl = 2NaCl + H_2O$

Of these metallic oxides, only the oxides of alkali metals (Na, K, etc.) and alkaline earth metals (Ca, Ba, etc.) dissolve in water and form soluble metallic hydroxides. These are called alkalis, which turn red litmus blue and react with acids forming salt and water.

$Na_2O + H_2O = 2NaOH$ $2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$
$CaO + H_2O = Ca(OH)_2$ $Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$

(iii) **Amphoteric oxides :** There are some oxides which react with both acids and alkalis forming salts and water. That is, these oxides exhibit both acidic and basic properties. These are called amphoteric oxides. aluminium oxide, Al_2O_3, reacts with dilute hydrochloric acid to yield aluminium chloride and water, and thus behaves as a basic oxide ;

$$Al_2O_3+6HCl=2AlCl_3+3H_2O$$

But with sodium hydroxide Al_2O_3 reacts as an acidic oxide and forms sodium aluminate,

$$Al_2O_3+2NaOH=2NaAlO_2+H_2O.$$

Oxides of weakly electropositive metals are usually amphoteric in character. Example are, ZnO, A $_2O_3$, SnO, Sb_2O_3, PbO etc.

$$ZnO+H_2SO_4=ZnSO_4+H_2O$$
$$ZnO+2NaOH=Na_2ZnO_2+H_2O$$

(sodium zincate)

$$PbO+2HNO_3=Pb\,(NO_3)_2+H_2O$$
$$PbO+2NaOH=Na_2PbO_2+H_2O$$

(sodium plumbite)

(iv) **Neutral oxides :** These oxides are neither acidic nor basic and give rise neither to acids, bases, nor salts. Familiar example are carbons monoxide (CO), nitrous oxide (N_2O) and nitric oxide (NO). Water (H_2O) is sometimes classified as a neutral oxide, but it is more accurately regarded as an amphoteric hydroxide of hydrogen, H (OH),

(v) **Higher oxides :** These include (a) peroxides, (b) dioxides or polyoxides and (c) super oxides.

(a) **Peroxides :** An oxide which gives hydrogen peroxide on being treated with dilute mineral acids in called a peroxide. Such as Na_2O_2, BaO_2 etc. A peroxide of an element contains more oxygen than what is present in its highest typical acidic or basic oxide.

$$Na_2O_2+2HCl=H_2O_2+2NaCl$$
$$BaO_2+H_2SO_4=H_2O_2+BaSO_4$$

True peroxides are formed by strongly electropositive alkali and alkaline earth metals and contain the oxygen chain—O—O—as in Na_2O_2 (Na-O-O-Na). A peroxide is eventually a salt of the weak acid hydrogen peroxide, H_2O_2 and is an electrovalent compound.

(b) **Dioxides or polyoxides :** A dioxide or a polyoxide is a covalent oxide of a weakly electropositive metal in which the metal is exerting a higher valency than it is in the basic oxide. Examples of these oxides are, PbO_2, MnO_2 etc. Though these oxides contain sufficient oxygen and have similar formulae as that of BaO_2, they are not classed as peroxides. This is because they do not possess the peroxide bridge—O—O—, as in the true peroxides and they do not yield H_2O_2 with dilute acids. When heated alone a dioxide evolves oxygen and leaves the basic oxide ; when heated with sulphuric acid it yields oxygen and the normal sulphate of the metal ; when heated with concentrated hydrochloric acid it evolves chlorine and gives the normal chloride of the metal.

$$2PbO_2 = 2PbO + O_2$$
$$2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O + O_2$$
$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$$

(c) **Superoxides :** Certain alkali and alkaline earth metal oxides contain higher proportion of oxygen and show close resemblemces with peroxids. They are called superoxides and do not belong to the true peroxide group as they contain O_2^- ion as in potassium superoxide (orange yellow solid), $K^+(O—O)^-$. When such oxides are treated with ice-cold water, they liberate oxygen with the formation of H_2O_2.

$$2KO_2 + 2H_2O = 2KOH + H_2O_2 + O_2$$
$$2NaO_2 + 2H_2O = 2NaOH + H_2O_2 + O_2$$

Superoxides are obtained by heating the corresponding peroxides with oxygen under high pressure and are the sources of oxygen of high altitude climbing.

(vi) **Mixed or compound oxides :** A compound or mixed oxide is formed by the combination of two simple oxides of the same element in which the element exhibits different valencies. These also produce a mixture of salts when acted upon by acids or alkalis. Thus Ferroso-ferric oxide (Fe_3O_4) is a mixed oxide of two basic oxides FeO and Fe_2O_3. It produces both ferrous and ferric chlorides with hydrochloric acid.

$$Fe_3O_4(FeO, Fe_2O_3)+8HCl=FeCl_2+2FeCl_3+4H_2O.$$

Red lead, Pb_3O_4 is a compound of a basic oxide and a dioxide, 2PbO, PbO_2. On reaction with dilute nitric acid, the basic oxide PbO is dissolved leaving an insoluble residue of the dioxide PbO_2 :—

$$Pb_3O_4(2PbO, PbO_2)+4HNO_3=2Pb(NO_3)_2+PbO_2+2H_2O$$

Other examples of mixed oxides are Mn_3O_4, N_2O_4 etc.

$$N_2O_4+2KOH=KNO_3+KNO_2+H_2O.$$

N.B. When an element yields more than one oxide, the oxides become more acidic as the valency of the element increases ; e.g., MnO strongly basic, Mn_2O_3 basic, MnO_2 amphoteric, MnO_3 acidic, Mn_2O_7 strongly acidic.

17.8. Preparation of oxides : There are different ways of preperation of oxides, some of which have already been discussed.

(1) Many oxides are formed when the elements are directly heated or burnt in air or oxygen,

$$C+O_2=CO_2 \qquad 2Mg+O_2=2MgO$$
$$P_4+5O_2=2P_2O_5 \qquad 2Cu+O_2=2CuO$$

(i) The thermal decomposition of nitrates, carbonates, hydroxides, etc. often produce oxides.

$$2Pb(NO_3)_2=2PbO+4NO_2+O_2$$
$$CaCO_3=CaO+CO_2$$
$$2Al(OH)_3=Al_2O_3+3H_2O$$
$$2FeSO_4=Fe_2O_3+SO_2+SO_3$$

(iii) Some elements are attacked by steam at elevated temperatures and give oxides,

$$3Fe+4H_2O=Fe_3O_4+4H_2 \qquad C+H_2O=CO+H_2$$

(iv) Certain metallic sulphides when roasted (strongly heated) in air also give the correoponding oxides,

$$2ZnS+3O_2=2ZnO+2SO_2 \qquad 4FeS_2+11O_2=2Fe_2O_3+8SO_2$$

(v) There are some metals which directly form their oxides when caustic soda solution is added to the aqueous solutions of their salts.

$$2AgNO_3+2NaOH=Ag_2O+2NaNO_3+H_2O$$

CATALYSIS

17·9 In the preparation of oxygen from potassium chlorate, it has been observed that the presence of MnO_2 facilitates the evolution of oxygen by increasing the rate of reaction. It is often found that the rates of many chemical reactions are likewise, influenced by the presence of a substance which remains chemically unaltered during the process—the rate of reaction may be either accelerated or (retarded.) The substance which influences the speed of the reaction, without being altered in mass and composition, is called a 'catalyst' and the phenomenon is known as 'catalysis'. MnO_2 acts as a catalyst in the preparation of oxygen. Almost every reaction can be catalysed by a suitable catalyst.

When the catalyst accelerats the rate of a reaction, it is called a 'positive catalyst'. When the catalyst retards the rate of the reaction it is called a 'negative catalyst'. Thus the rate of decomposition of H_2O_2 is accelerated in presense of pt-black which acts as a positive catalyst. Again its decomposition rate can be reduced by adding small amount of dilute H_2SO_4 which acts as a negative catalyst or an inhibitor.

A few examples of Catalysed reactions are given below :

Reatction	Catalyst	Nature of Catalysis
1. $2SO_2+O_2=2SO_3$	NOgas (or Pt or V_2O_5)	Positive
2. $N_2+3H_2=2NH_3$	Fe	Positive
3. $2KClO_3=2KCl+3O_2$	MnO_2	Positive
4. $4NH_3+5O_2=4NO+6H_2O$	Pt	Positive
5. (a) $2H_2O_2=2H_2O+O_2$	Pt-black	Positive
(b) $2H_2O_2=2H_2O+O_2$	H_2SO_4 (H^+ ions)	Negative
6. (a) $2Na_2SO_3+O_2=2Na_2SO_4$	Cu^{++}ions	positive
(b) $2Na_2SO_3+O_2=2Na_2SO_4$	glycerol	Negative
7. $2H_2+O_2=2H_2O$	CO	Negative

The catalysed reactions have the following characteristics :—

(i) The catalyst remains unchanged chemically at the end of the reaction.

(ii) A very small amount of catalyst is sufficient to effect an appreciable change in the velocity of a reaction.

(iii) A catalyst cannot start a reaction, it can only increase or decrease the speed of the reaction.

(iv) The position of equilibrium in a reversible reaction is unaffected by the presence of a catalyst. It influences the direct and the reverse reaction to an equal extent.

Exercise—17

1. (a) Describe the labratory method for the preparation of pure oxygen, By what tests would you confirm that the residue left is potassium chloride.

(b) Discuss the importance of MnO_2 in the preparation of oxygen form potassim chlorate.

2. How is oxygen produced on a large scale from (i) air and (ii) water ? What are the most important uses of the gas ?

3. What changes would occur when the following are heated ? (i) mercuric oxide. (ii) potassium nitrate, (iii) $Cu(NO_3)_2$; (iv) Ammonium nitrate, (v) potassium permanganate. Give equations

4. How and under what conditions would oxygen react with, (i) nitrogen, (ii) sodium, (iii) nitric oxide, (iv) ammonia, (v) sulpher dioxide, Give equations.

5. (a) What are oxides ? How would you classify them ? Give examples.

(b) an oxide has the formula MO_2. How may it be determined if this is (i) a dioxide, (ii) a peroxide or iii a superoxide ;

6. Write notes on :—

(i) Isotopes of oxygen, (ii) negative catalysis, (iii) amphoteric oxide, (iv) photosynthesis.

7. Write a brief note on "catalysis". Give two examples for each of positively catalysed and negatively catalysed reactions

8. How will you obtain a sample of oxygen frnm (i) sodium peroxide (ii) lead nitrate ! Sketch the apparatus used.

CHAPTER XVIII

OXIDATION AND REDUCTION

Oxidation and reduction reactions are two special types of chemical reactions. Such reactions are of great importance as they reveal the mode of involvement of electrons in chemical reactions.

18.1. Oxidation :—The term oxidation is ordinarily used to describe reactions in which oxygen is directly added to a substance. For example :—

(1) $C+O_2=CO_2$ (3) $2Na_2SO_3+O_2=2Na_2SO_4$

(2) $Mg+O_2=2MgO$ (4) $PbS+4H_2O_2=PbSO_4+4H_2O$

Since oxygen is an electronegative element, the term 'oxidation' has been extended to include all reactions in which there is an addition of electronegative element (Such as sulphur or chlorine) or radical (e.g. sulphate). for example—

(5) $2Na+Cl_2=2NaCl$ (7) $2FeCl_2+Cl_2=2FeCl_3$

(6) $C+2S=CS_2$ (8) $2FeSO_4+H_2SO_4+H_2O_2=$ $Fe(SO_4)_3+2H_2O$

The ratio of the electronegative (non-metallic) to the electropositive (or metallic) atoms or groups in a substance, is increased in oxidation. The removal of hydrogen or the metallic part (i.e. the electropositive atom or radical) from a compound also increases this ratio. So the removal of hydrogen or of electro-positive element or radical from a substance is also regarded as oxidation. For example—

(9) $H_2S+Br_2=S+2HBr$ (11) $2KI+H_2O_2=I_2+2KOH$

(10) $2NH_3+3Cl_2=N_2+6HCl$ (12) $2HBr+H_2SO_4=Br_2+$ SO_2+2H_2O

Thus, to define :

Oxidation is a process which involves (i) addition or increasing the proportion of oxygen (or any electronegative element or radical) *to a substance (an element or a compound) or (ii) removal or decreasing the proportion of hydrogen (or any electropositive element or radical) from a compound.*

18.2. **Reduction :**—The process of reduction is the converse of oxidation. The ratio of the metallic or electropositive to the non-metallic or electronegative atoms or groups in a substance is increased in reduction process.

Therefore, to define :

Reduction is a process which involves (i) addition or increasing the proportion of hydrogen (or any electropositive element or radical) to a substance (an element or a compound) or (ii) removal or decreasing the proportion of oxygen (or any electronegative element or radical) from a compound.

Examples :—

a) Addition of hydrogen—

(13) $Cl_2+2H_2S=2HCl+S$ (14) $N_2+3H_2=2NH_3$

b) Addition of electropositive element.—

(15) $2CuCl_2+SO_2+2H_2O=Cu_2Cl_2+H_2SO_4+2HCl$

(16) $2HgCl_2+SnCl_2=Hg_2Cl_2+SnCl_4$

c) Removal of oxygen.—

(17) $CuO+H_2=Cu+H_2O$ (18) $Fe_2O_3+3C=2Fe+3CO$

d) Removal of electronegative element or radical—

(19) $2FeCl_3+H_2S=2FeCl_2+S+2HCl$

(22) $Fe_2(SO_4)_3+2H=2FeSO_4+H_2SO_4$.

18.3. **Oxidising and Reducing Agents** : A substance which is capable of causing another substance to be oxidised is called an *oxidising agent*. Thus in equation (7) above, chlorine causes the oxidation of $FeCl_2$ by the addition of electronegative element chlorine, hence chlorine is the oxidising agent here. Again in equation (12) sulphuric acid is responsible for the oxidation of HBr to bromine by removing hydrogen, hence it is functioning as an oxidising agent.

Likewise, a substance which is capable of causing another substance to be reduced is called a reducing agent. Thus in equation (18) above, carbon reduces Fe_2O_3 into metallic iron by removing oxygen, hence carbon here acts as a reducing agent. Again in equation (19), H_2S reduces ferric chloride to ferrous chloride by decreasing the proportion of electronegative chlorine, hence H_2S is a reducing agent.

Example of common oxidising agents are—Oxygen, ozone, hydrogen peroxide, nitric acid, halogens, potassium permanganate, potassium dichromate, etc.

Example of common reducing agents are—Nascent hydrogen, hydrogen gas, hydrogen sulphide, hydrogen iodide, sulphurdioxide, stannous chloride, carbon, carbon monoxide, phosphorus, glucose etc.

18.4. **Redox Reactions** :—When an oxidising agent causes the oxidation of another substance, say by adding oxygen or by taking away hydrogen, the agent itself must be reduced. That is the oxidising agent gets reduced in the process of oxidation.

Again, a reducing agent, while causing the reduction of another substance, takes away oxygen or supplies hydrogen and there by gets itself oxidised. That is, in the process of reduction, the reducing agent gets oxidised.

It is hence said :

The processes of oxidation and reduction are complementary and take place simultaneously.

These reactions are therefore called **Redox Reactions.**

Illustrations :—

(1) The reaction : $PbS + 4H_2O_2 = PbSO_4 + 4H_2O$.

Here PbS is oxidised as oxygen is added to PbS. The oxidising agent H_2O_2 loses oxygen and is reduced to water. Hence the reaction involves the oxidation of PbS and the reduction of H_2O_2.

(2) The reaction : $CuO + CO = Cu + CO_2$.

Here CuO is reduced to metallic copper as oxygen is removed.

The reducing agent CO is oxidised to CO_2 by taking up oxygen. Hence the reaction involves the oxidation of carbonmonoxide and the reduction of CuO.

(3) The reaction : $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$.

Here ferric chloride is reduced to ferrous chloride since the proportion of electronegative chlorine has diminished. The reducing agent $SnCl_2$ has been oxidised to $SnCl_4$ due the iucrease in the proportion of chlorine. Again, when one ($FeCl_3$) is redueed, the other ($SnCl_2$) is oxidised.

Such behaviour is observed in all oxidation or reduction reactions.

18.5. Redox Reactions from Electronic Concept : The limitations of the earlier concepts of oxidation and reduction had been realised for a long time. The electronic concept gives a logical interpretation of oxidation and reduction. Many Redox Reactions, especially involving ionic compounds, can be clearly and efficiently explained in terns of the transfer of electrons occurring in them.

Let us take an illustration ; (1) Ferrous chloride is oxidised to ferric chloride by chlorine in an aqueous solution : $2FeCl_2 + Cl_2 = 2FeCl_3$, or expressed ionically, $2Fe^{++} + Cl_2 = 2Fe^{+++} + 2Cl^-$

In the redox process, the ferrous ion Fe^{++} is oxidised to the ferric ion Fe^{+++} by loss of an electron and chlorine atom is reduced to negatively charged chloride ion Cl^- by accepting the electron. Oxidation : $Fe^{++} - e = Fe^{+++}$, Reduction : $Cl + e = Cl^-$.

(2) In the reaction : $H_2S + Br_2 = S + 2HBr$ or, expressed ionically, $S^{--} + Br_2 = S + 2Br^-$. H_2S has been oxidised to sulphur and Br_2 has been reduced to HBr. In fact, sulphide ion S^{--} has lost its two electrons to be oxidised to sulphur and each bromine atom has accepted an electron to be reduced to Br^- ion, that is, Oxidation : $S^{--} - 2e = S$, Reduction $Br_2 + 2e = 2Br^-$.

This leads to the view that *oxtdation is a process which involves loss of one or more electrons by atoms or ions, whereas reduction is a process which results in the gain of one or more electrons by the atoms or ions.*

Since a redox reaction involves both oxidation and reduction, one of the participant loses electrons (reducing agent or reductant) and the other accepts the electrons (oxidising agent or oxidant). The loss of electrons by reductant must be equal to the gain of electrons by the oxidant. Thus, considering the number of electrons exchanged in the redox reaction : $Sn^{++} \rightleftharpoons Sn^{++++} + 2e$; $Fe^{+++} + e \rightleftharpoons Fe^{++}$, the balanced equation is $Sn^{2+} + 2Fe^{3+} \rightleftharpoons Sn^{4+} + 2Fe^{2+}$. All redox reactions are thus justifiedly regarded as a combination of two half (or partial) reactions, one involving only oxidation and the other only reduction :

It is evident that oxidation involves an increase of positive valency due to loss of electrons, while decrease in positive valency (or increase in negative valency) results from gain of electrons in reduction. Many reactions which are not usually regarded as oxidation-reductions, are in fact redox reactions from electronic standpoint. For example,

1. Displacement of copper from copper sulphate by zinc,

$$CuSO_4 + Zn = ZnSO_4 + Cu$$

$$\text{or, } Cu^{++} + Zn = Zn^{++} + Cu$$

$$\text{Hence } Cu^{++} + 2e = Cu \text{ (reduction)}$$

$$Zn - 2e = Zn^{++} \text{ (oxidation)}$$

2. Evolution of hydrogen when Mg reacts with HCl.

$$Mg + 2HCl = MgCl_2 + H_2.$$

$$\text{or, } Mg + 2H^+ = Mg^{++} + H_2$$

It consists of two simultaneous changes,

$$Mg - 2e = Mg^{++} \text{ (oxidation)}$$

$$2H + 2e = H_2 \text{ (reduction)}$$

That this concept of electron-transfer in redox reactions is true and that such reactions consist or two simultaneous changes, can be experimentally demonstrated as follows :—

Consider the above reaction between zinc and copper-sulphate olution : $CuSO_4 + Zn = ZnSO_4 + Cu$.

In this reaction, as already stated, zinc is oxidised to Zn^{++} ion (as $ZnSO_4$) and Cu^{++} ion is reduced to metallic copper, the two-half reactions are :

(i) $Zn \rightarrow Zn^{++} + 2e$ (oxidation)
(ii) $Cu^{++} + 2e \rightarrow Cu$ (reduction)

The two-half reactions may be made to occur separately by placing a zinc rod in a beaker containing $ZnSO_4$ solution and a copper rod in a beaker containing $CuSO_4$ solution. (Fig 18.1). The two solutions are connected by a salt bridge (shown as an inverted U-tube) and the two rods are externally connected through a variable resistance by a conducting wire When the circuit is closed, a current flows through the conducting wire After a few minutes, it will be found that the copper rod gradually gains in weight while the zinc rod gradually loses weight. The increase in weight of the copper rod is due to the deposition of metallic copper from $CuSO_4$ solution through its reduction ($Cu^{++} \rightarrow Cu$) and the zinc rod loses its weight due to the dissolution of zinc as zinc sulphate through its oxidation ($Zn \rightarrow Zn^{++}$) ; the electrons lost by zinc during oxidation are transferred through the connecting wire to the Cu^{++} ions, which are reduced by accepting them. Thus, the same redox effects are obtained by keeping the two agents (oxidant and reductant) not in direct contact with each other. In other words, the two-half reactions (one of oxidation and the other of reduction), carried out separately, give on combination the total redox reaction which really involves electron-transfer.

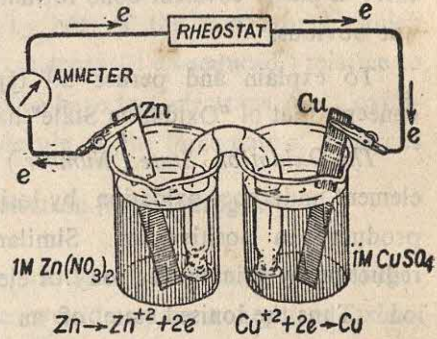


Fig 18 1 Displacement of copper by zinc form $CuSO_4$ solution

18 6. The state of oxidation : Oxidation Number : In certain reactions the electron transfer does not follow a clear pattern. For example, the redox reaction :

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

In such cases, it is difficult to visualise the loss or gain of electrons. How MnO_4^- ion has been transformed into Mn^{++} ion is not immediately obvious.

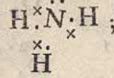
Besides, there are other reactions involing non-ionic compounds, such as $C+O_2=CO_2$, where acceptance or loss of electrons cannot be conceived. In the combination of hydrogen with chlorine there is partly covalent bond formation and electron loss or gain is not obvious.

To explain and peruse all types of redox reactions, a new coneept, that of "Oxidation State" has now been in'rodnced.

The Oxidation State (Number) : It is evident that when an element undergoes oxidation by losing electron (or electrons), the product is a positive ion. Similarly when an element undergoes reduction by gaining electron (or electrons),the product is a negative ion. Thus the ionised state of an element is either the oxidised state or the reduced state—the elemental state being regarded as a state of zero oxidation. The *Oxidation State* of an element present in a compound is determined from the number of electrons lost or gained by it relative to its elemental state and it is expressed in terms of oxidation number. That is, the oxidation number of the element in a particular compound denotes the extent of oxidation or reduction necessary to change the element from the free state into that in the compound. Oxidation number is positive if oxidation is required to effect the change and negative if reduction is necessary. Thus (i) in NaCl [$NaCl \rightleftharpoons Na^+ + Cl^-$], the oxidation number (state) of sodium is $+1$ (by losing one electron) and that of chlorine is -1 (by taking up one electron).

(ii) in $CaCl_2$ [$CaCl_2 \rightleftharpoons Ca^{++} + 2Cl^-$], the oxidation number of calcium is $+2$ and that of chlorine is -1.

The determination of oxidation number is simple and is easily understood in case of ionic compounds where direct transfer of electrons (s) takes place. But in case of covalent compounds where the elements are bound by shared electron-pairs and not by direct transfer of electron (s), the oxidation state of an element in the compound is difficult to be visualised. In such cases the oxidation number is determined by the number of electron-pairs shared by the particular atoms. But in covalent compounds composed of like atoms (e. g. H_2, O_2, Cl_2, N_2 etc. i.e. elements in the molecular state), the electron pairs are equally shared between the two atoms, their oxidation number is supposed to be zero. In case of covalent compounds composed of unlike atoms, the electron pair is shared to a greater extent by one of the two atoms, which will be supposed to have gained electrons (i,e, reduced) relative to the other, which will then be said to have lost electrons (i. e. oxidised). For example, in NH_3 molecule, of the three pair of electrons

[
$H\overset{\times}{\underset{\cdot}{:}}\overset{\cdot\cdot}{N}\underset{\times}{\cdot}H \underset{\overset{\times\cdot}{H}}{}$; $^{\circ}$ electron from N, x electron from hydrogen]

major share is taken by nitrogen (nitrogen being more electronegative than hydrogen). So nitrogen would assume a negative oxidation state. Hence in NH_3, the oxidation state of each hydrogen is $+1$, and that of nitrogen is -3. Hence the oxidation number of an atom in a covalent molecule is determined by the number of electron-pair of which the atom has taken less share (positive oxidation number) or greater share (negative oxidation number).

From the above discussions, the guiding principles for the determination of oxidation number of an element present in a compound may be summerised as follows :

(1) The oxidation number in the elementary state is zero.

(2) The oxidation number of simple ions (in which only one element is present) such as Na^+, Mg^{++}, Cl^- etc, is equal to the charge on the ion (i. e. electrovalency) with proper sign. The oxidation number of Mg^{++} is $+2$, that of Cl^- is -1.

(3) The oxidation number of combined hydrogen (other than H_2) is always $+1$, except in ionic hydrides (e. g. in NaH), where it is -1.

(4) The oxidation number of combined oxygen (other than O_2 and O_3) is normally -2, except in H_2O_2 or other peroxides, where it is -1.

(5) The oxidation number of an atom of any element in a a covalent molecule (other than its own molecule) is equal to the charge that it would acquire it the shared electron-pair is assigned completely to the more electronegative one of the two atoms sharing them.

(6) The algebraic sum of the oxidation numbers of all the elements present in a molecule, each multiplied by the number of respective atoms is always 'zero'.

Thus putting the oxidation numbers overhead, this may be easily verified.

$$\overset{+1\times2}{H_2}\quad \overset{+6\times1}{S}\quad \overset{-2\times4}{O_4}\ ;\qquad \overset{+1\times1}{K}\quad \overset{+5\times1}{Cl}\quad \overset{-2\times3}{O_3}$$

$$\overset{+1\times1}{K}\quad \overset{+5\times1}{N}\quad \overset{-2\times3}{O_3}\ ;\qquad \overset{+1\times3}{Na_3}\quad \overset{+5\times1}{P}\quad \overset{-2\times4}{O_4}$$

(7) The charge of an ionic radical is the algebraic sum of the oxidation numbers of the elements present in the radical ;

$$[\overset{+6}{S}\ \ \overset{-2\times4}{O_4}]^{--}\ ;\quad [\overset{+4}{C}\ \ \overset{-2\times3}{O_3}]^{--}\ ;\quad [\overset{+5}{N}\ \ \overset{-2\times3}{O_3}]^{-}\ \text{etc.}$$

With the help of these rules, it is easy to ascertain the oxidation number of an element in a compound.

Exercise : Find out the oxidation number of (i) Mn in $KMnO_4$; (ii) Cr in $K_2Cr_2O_7$; (iii) N in HNO_3 ; (iv) Cl in $Ca(ClO_3)_2$

(i) Let the oxidation number of Mn be x, then

$$\overset{+1}{K}\ \overset{x}{Mn}\ \overset{-2\times4}{O_4}\ ;\ \text{i. c. } 1+x-8=0 \quad \therefore\ x=+7.$$

That is, in $KMnO_4$, the oxidation number of Mn $=+7$.

(ii) Suppose the oxidation number of Cr by y, then

$$\overset{+1\times2}{K_2}\quad \overset{y\times2}{Cr_2}\quad \overset{-2\times7}{O_7}\ ;\ \text{i. c. } 2+2y-14=0, \text{ or } y=+6.$$

Therefore the oxidation number of Cr in $K_2Cr_2O_7$ is $+6$.

(iii) Let the oxidation number of N is z, then

$$\overset{+1}{H}\ \overset{z}{N}\ \overset{-2\times3}{O_3}\ ;\ \text{i. c. } 1+z-6=0 \quad \therefore\ z=+5.$$

Hence, in HNO_3, the oxidation number of N is $+5$.

(iv) Suppose the oxidation number Cl is p, then

$$Ca(ClO_3)_2 \text{ i.e } \overset{+2\times1}{Ca} \quad \overset{p\times2}{Cl_2} \quad \overset{-2\times6}{O_6}; \quad \text{i.e. } 2+2p-12=0$$

$$\therefore \; p=+5.$$

Therefore, the oxidation number of chlorine in calcium chlorate is +5.

Many elements, especially those of groups V, VI, and VII and of the transitional series, have different oxidation numbers in different compounds indicating their different states of oxidation. The oxidation numbers of nitrogen, sulphur and chlorine are tabulated below.

Nitrogen		Sulphur		Chlorine	
Compound	oxidation number	Compound	oxidation number	Compound	oxidation number
N_2O_5	+5	SO_3	+6	$KClO_4$	+7
NO_2	+4	SO_2	+4	$KClO_3$	+5
N_2O_3	+3	S	0	ClO_2	+4
NO	+2	Na_2S_2	−1	Cl_2O	+1
N_2O	+1	H_2S	−2	Cl_2	0
N_2	0			HCl	−1
NH_3	−3				

The redox reaction are characterised by the following conditions.

(i) During a reaction, if the oxidation number of an element is increased it is said to be oxidised. It the oxidation number of an element is decreased, it is said to be reduced, These are often called key-elements.

(2) the net decrease in the oxidation number of the key element in the oxidant, undergoing reduction must be equal to the net increase in the oxidation number of the key element In the reducdant, undergoing oxidation.

For example :—

(i) $\overset{0}{Zn}+\overset{+1}{H}_2SO_4=\overset{+2}{Zn}SO_4+\overset{0}{H}$

Hence the increase in oxidation number of Zn (reductant) $= +2 - 0 = 2$ and the decrease in oxidation number of H (H_2SO_4 being oxidant) $= +2 - 0 = 2$

(ii) $H_2\overset{-2}{S} + \overset{0}{Br}_2 = \overset{0}{S} + 2H\overset{-1}{Br}$.
Increase in oxidation number of $S = 0 - (-2) = 2$

and decrease in the oxidation number of $Br = 0 - (-2) = 2$

This is the characteristic of all redox reactions

18.7. Use of Oxidation Number in Balancing Redox Reactions.

It has already been mentioned that all redox reactions involve changes of oxidation number, the oxidation number of some element will decrease while that of another will increase. The net increase and net decrease will have to be equal, since oxidation must exactly compensate reduction. If the reactants and resultants are known, oxidation numbers would provide a good basis for balancing redox reactions. In balancing such equations, the following steps are to be followed :—

(i) The key element in the oxidant and also in the reductant, which change their oxidation numbers in the reaction are to be found out.

(ii) The increase in oxidation number for one element is then made equal to the decrease in oxidation number for another by multiplying with suitable coefficients.

(iii) finally the equation is balanced by inspection.

Some examples are given to illustrate the method.

a) Hydrochloric acid is oxidised to chlorine by MnO_2 and manganous chloride is formed.

$$\overset{+4}{Mn}O_2 + H\overset{-1}{Cl} \rightarrow \overset{0}{Cl}_2 + \overset{+2}{Mn}Cl_2 + H_2O \text{ (unbalanced)}$$

Here the oxidant is MnO_2 and the key element which suffers a change in the oxidation number ia Mn.

Oxidation number of Mn in MnO_2 is $+4$ and in $MnCl_2$ is $+2$ So Mn has suffered a decrease in oxidaion number by 2 units. Again the reductant is HCl and the key element is Cl.

The oxidation number of Cl in HCl is -1 and in the elemental state, Cl_2 is 0.

$\therefore$ Cl has suffered an increase in its oxidation number bv 1 unit.

So to make the changes in oxidation numbers equal, MnO_2 and HCl should react in the molecular ratio 1 : 2,

i. e., $MnO_2 + 2HCl \rightarrow Cl_2 + MnCl_2 + H_2O$ (unbalanced)

However, since the product is $MnCl_2$, it is obvious that two more chloride ions (i. e. two more molecules of HCl) will be required to balance the equation. Thus.

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O \text{ (balanced)}$$

(b) Action of hot concentrated sulphuric acid on carbon.

$$\overset{0}{C} + H_2\overset{+6}{S}O_4 \rightarrow \overset{+4}{C}O_2 + \overset{+4}{S}O_2 + H_2O \text{ (unbalanced)}$$

Here C is oxidised to CO_2 and H_2SO_4 is reduced to SO_2.

The increase in oxidation number of $C = 4$

and the decrease in oxidation number of $S = 2$

To make the changes in oxidation numbers equal, proportion of C and H_2SO_4 must be 1 to 2.

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O \text{ (balanced)}$$

(c) Aluminium reacts with HCl producing $AlCl_3$ and hydrogen.

$$\overset{0}{Al} + \overset{+1}{H}Cl \rightarrow \overset{+3}{Al}Cl_3 + \overset{0}{H_2} \text{ (unbalanced)}$$

The increase in oxidation number of $Al = 3$

and the decrease in oxidation number of $H = 1$

$\therefore$ To equalise the changes in oxidation numbers, for each Al atom three HCl molecules would be needed.

$$Al + 3HCl \rightarrow AlCl_3 + \tfrac{3}{2} H_2$$

$$\text{or, } 2Al + 6HCl = 2AlCl_3 + 3H_2 \text{ (balanced).}$$

(d) $SnCl_2$ reduces $FeCl_3$ to $FeCl_2$, and is itself oxidised to $SnCl_4$.

decrease in ox. no. by 1

$$\overset{+3}{Fe}Cl_3 + \overset{+2}{Sn}Cl_2 \rightarrow \overset{+2}{Fe}Cl_2 + \overset{+4}{Sn}Cl_4$$

increase in ox. no. by 2

To make the decrease and the increase in oxidation numbers equal, $FeCl_3$ and $SnCl_2$ must be in the proportion of 2 : 1.

So, the balanced equation is

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

(e) Moderately concentrated nitiric acid reacts with copper producing copper nitrate, nitiic oxide and water.

increase in ox no. by 2

$$\overset{0}{Cu} + H\overset{+5}{N}O_3 \rightarrow \overset{+2}{Cu}\,(NO_3)_2 + \overset{+2}{N}O + H_2O \text{ (unbalanced)}$$

decrease in ox no. by 3

Hence for producing NO, for three atoms of Cu, two molecules of HNO_3 would be required.

$$3Cu + 2HNO_3 \rightarrow 3Cu\,(NO_3)_2 + 2NO + H_2O \text{ (unbalanced).}$$

To convert the three atom of copper to the nitrate additional 6 molecules of HNO_3 would be necessary. Hence the appropriate equation would be :

$$3Cu + 8HNO_3 = 3Cu\,(NO_3)_2 + 2NO + 4H_2O \text{ (balanced)}$$

(f) Acidified $KMnO_4$ solution oxidises H_2S to sulphur.

$$K\overset{+7}{Mn}O_4 + H_2SO_4 + H_2\overset{-2}{S} \rightarrow K_2SO_4 + \overset{+2}{Mn}SO_4 + \overset{0}{S} + H_2O \text{ (unbalanced)}$$

The decrease in oxidation number of $Mn = 7 - 2 = 5$

and the increase in oxidation number of $S = 0 - (-2) = 2$

To Make the changes in oxidation number equal ; the ratio of $KMuO_4$ to H_2S must be 2 : 5. This makes the equation

$$2KMnO_4 + 5H_2S + H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5S + H_2O$$

Equating $(SO_4)^{--}$ on both sides, and balancing the equation by inspection,

$$\therefore\ 2KMnO_4 + 5H_2S + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5S + 8H_2O.$$

(g) $K_2Cr_2O_7$ in presence of dilute H_2SO_4 oxidises potassium iodide liberating iodine.

$$K_2\overset{+6}{Cr_2}O_7+H_2SO_4+K\overset{-1}{I}\rightarrow K_2SO_4+\overset{+3}{Cr_2}(SO_4)_3+\overset{0}{I_2}+H_2O$$

The decrease in the oxidation number of Cr = 3

and the increase in the oxidation number of I = 1

Hence, to equalise the changes in oxidation numbers, 6 I atoms are needed for 2 Cr atoms.

$$K_2Cr_2O_7+6KI+H_2SO_4\rightarrow 4K_2SO_4+Cr_2(SO_4)_3+3I_2+H_2O$$

Equating $(SO_4)^{--}$ on both sides and finally balancing the equation by inspection,

$$K_2Cr_2O_7+7H_2SO_4+6KI=4K_2SO_4+Cr_2(SO_4)_3+3I_2+7H_2O$$

(h) Ammonia passed over red hot CuO gives metallic copper, nitrogen and steam.

dicrease in
ox. no. by 2

$$\overset{-3}{N}H_3+\overset{+2}{Cu}O\longrightarrow\overset{0}{Cu}+\overset{0}{N_2}+H_2O$$

increase in ox. no by 3

∴ to equalise the change in oxidation numbers the ratio of NH_3 to CuO must be 2 : 3.

$$2NH_3+3CuO=3Cu+N_2+3H_2O \text{ (balanced)}$$

18.8. Disproportionation : There are reactions in which the molecules of the same compound undergo simultaneous self-oxidation and reduction. That is, a portion of the molecule is oxidised and a portion reduced. This is called "Disproportionation". For example ;

(1) When carbon-monoxide heated to a high temperature, it suffers self-oxidation and reduction, i.e. disproportionation occurs.

$$2\overset{+2}{C}O=\overset{0}{C}+\overset{+4}{C}O_2$$

(2) Nitrous acid when heated suffers disproportionation.

$$3H\overset{+3}{N}O_2=H\overset{+5}{N}O_3+2\overset{+2}{N}O+H_2O$$

18.9. Equivalent weights of oxidising and reducing agents :—

The equivalent weights can easily be obtained by dividing the molecular weight of the oxidising or reducing agent by the net change in oxidation number per molecule thus.

(1) For $K\overset{+7}{Mn}O_4 \rightarrow \overset{+2}{Mn}SO_4$

The change in oxidation number = 5

$\therefore$ Equivalent weight of $KMnO_4$

$$= \frac{\text{Mol. wt. of } KMnO_4}{5} = \frac{158}{5} = 31{\cdot}6$$

(ii) For $K_2\overset{+6}{Cr}_2O_7 \rightarrow \overset{+3}{Cr}_2\ (SO_4)_3$

The change in oxidation number per molecule $= 2 \times 3 = 6$

$\therefore$ Eq. Wt. of $K_2Cr_2O_7 = \frac{\text{Mol. wt.}}{6} = \frac{294}{6} = 49$. etc. etc.

Exercise—18

1. Explain clearly, with illustration, the meaning of "oxidation and reduction".

2. Oxidation and reduction are complimentary processes—Explain with suitable illustrations.

3. Define and illustrate oxidising and reducing agents. Illustrate the oxidising or reducing action of the following :—Sulphuric acid, Chlorine, hydrogen sulphide, nitric acid, hydrogen peroxide, Sulpher dioxide, Stannous chloride.

4. Is it necessary that an oxidising agent should contain oxygen ? Give your reasons.

5. Explain "oxidation and reduction" form the concept of the electonic theory.

6. What is meant by the oxidation number of an element ? Find out the oxidation number of (i) Cr in K_2CrO_4, (ii) P in PH_3 and H_3PO_4, (iii) H in LiH, (iv) Cl in HClO, (v) Mn in $CaMnO_4$.

7. Explain how does oxidation number method help in balancing redox equations. Give the underlying principles of the method and illustrate with reference to the reactions between

(i) Hydrogen sulphide and sulpher dioxide,
(ii) Hydrogen bromide and sulphuric acid,
(iii) acidified $KMnO_4$ solution and potassium iodide solution,
(iv) acidified $K_2Cr_2O_7$ solution and ferrous sulphate solution.
(v) acidified KI solution and H_2O_2
(vi) Iodine and sodium thiosulphate.
(vii) Copper and conceutrated nitrc acid.
(viii) acidified $KMnO_4$ solution and $FeSO_4$ solution.

Give the balanced equation in each case.

CHAPTER XIX

WATER

Hydrogen and oxygen form two compounds between them : (1) Water, H_2O and (2) Hydrogen peroxide, H_2O_2. The Chemistry of water will be discussed in this chapter, that of hydrogen peroxide will be described later.

19.1. History and occurrence :—Until the time of Cavandish, water was regarded to be an element. But in 1781, Cavandish proved that water was a compound and obtained it by exploding a mixture of hydrogen and oxygen in the ratio of 2 : 1 by volume. The same conclusion was also drawn by Lavoisier in 1783.

Water occurs abundantly in nature (i) as water vapour in the atmosphere, (ii) as liqid water in the ocean and seas and as inland waters and (iii) in the solid state (ice) on some mountain peaks and glaciers and in polar regions. Nearly 70·8% of earth's surface is covered with water. Besides, a major portion of animal and plant bodies consists of water. There is more than 60% water in human bodies. A good quantity of water is locked in natural crystalline solids and minerals as water of crystallisation.

19·2. Natural waters : Water found in nature is never chemically pure. Natural waters are liable to contain many impurities both soluble and suspended—their nature and amount vary with the source from which waters are obtained. Hence natural waters may be classified according to their sources as (a) rain water, (b) river water, (c) spring and well water, (d) sea water.

(a) Rain water :—The purest form of natural water is rain water. It contains in solution small quantities of atmospheric gases like oxygen, nitrogen and carbondioxide and traces of ammonium nitrate and nitric acid formed by electrical dischargesduring thunderstorms. Rain water falling over towns is liable to contain, in solutions, oxides of sulphur formed from the burning of sulphuriferrous coal.

(b) **River water** :—Rivers are generally fed by rain water. While flowing over the earth's surface the river water comes in contact with different rocks and soils and thereby collects suspended impurities like clay particles and contains many dissolved impurities like chlorides, sulphates, bicarbonates and carbonates of sodium, calcium, magnesium and iron. River water can be used for drinking purposes after freeing it from suspended and harmful ingredients.

(c) **Spring and well water** :—The portion of rain water which percolates through the soil gives rise to spring and well water. Due to natural filtration through porous strata of the soil, the suspended particles are removed, but the amount of the dissolved materials is increased. Such water is often suitable as drinking water because it is free from orgainc matter which are oxidised by soil bacteria. The spring water sometimes contains an excess of mineral matter, and is then called *mineral water* The mineral waters have special tastes and often possess curative and medicinal values.

Sea water :—Of all natural waters, sea water happens to be the largest in amount, but it contains the maximum amount of dissolved impurities, about 3·6%on the average, of which 2·6%iscommon salt. Sea water is unsuitable for drinking and other domestic work.

19·3. Hardness of water : Hard and Soft water.

According to their behaviour towards soaps, the natural waters have been classified into two groups (1) Soft water and (2) Hard water.

Soft water : The water which readily produces lather of films and froths when agitated with a soap solution is known as '*soft water.*

Hard water : Water which is reluctant to yield a lather when agitated with soap solution is said to be '*hard water*'. Hard water does not produce lather until a considerable amount of soap has been used up.

The hardness of water arises due to the presence of soluble salts like chlorides, sulphates, and bicarbonates of calcium, magnesium and iron in water. The chlorides and sulphates are directly dissolved from the earth's surface by the flowing water. The bicarbonates are formed by the action of dissolved CO_2 on the carbonates present in the earth ; eg.

$$H_2O+CO_2=H_2CO_3\ ;\quad H_2CO_3+CaCO_3=Ca(HCO_3)_2.$$

Behaviour of hard water towards soaps ;

Soaps ordinarily used are sodium and potassium salts of long-chain fatty acids like oleic, stearic, palmitic acids ; they are soluble in water. The surface tension of water is markedly lowered by the presence of soap in solution and consequently a soap solution when shaken produces a stable lather of films and bubbles. But when these soaps are added to hard water, the soaps react with soluble calcium, magnesium or iron salts present and produce insoluble slimy precipitates of calcium, magnesium or iron stearate, oleate or palmitates. These salts do not produce lather and separate as a scum. The result is soap is wasted and no lather (necessary for cleaning purpose) is formed.

$$\underset{\substack{\text{sodium stearate}\\\text{(soluble Soap)}}}{2C_{17}H_{35}COONa}+CaSO_4=\underset{\substack{\text{calcium stearate}\\\text{(insoluble pptt.)}}}{(C_{17}H_{35}COO)_2Ca}+Na_2SO_4$$

When all the calcium, magnesium, iron salts are removed as insoluble precipitate, only then the soap would produced lather with this water.

Difficulties with hurd warer : (1) Hard water is unsuitable for laundry purposes as much soap is wasted during washing with hard water.

(ii) Hard water is not suitable for boilers where steam is generated for industrial purposes. The use of hard water in boilers results in the deposition of thick, heat-insulating scales of carbonates and sulphates of calcium and magnesium on the walls of the boiler. As a result more fuel is needed for heating and rapid deterioration of boilers due to over-heating take place.

(iii) Very hard water is unsuitable for cooking and drinking purposes.

(iv) Hard water cannot be used in paper industries and in many dyeing industries.

For these dtfficulties, hardness has to be removed before the water is used. This operation of removal of hardness is called "softening of water".

Classification of hardness of water : For convenience hardness of water is classified (i) temporary and (ii) permanent.

The hardness of water is said to be *temporary* when the hardness can be removed by easy means like boiling etc. *Temporary hardness* is due to the presence of bicarbonates of calcium, magnesium and iron in water.

The hardness of water is said to be *permanent* when the hardness cannot be removed easily by mere boiling. *Permanent hardness* is due to the presence of chlorides and sulphates of calcium, magnesium and iron in water.

19.4. Removal of Hardness—Softening of Hard Water.

Principle : It is clear that the hardness of water is due to the presence of soluble salts of calcium, magnesium or iron in water. If by any method these soluble salts are converted into insoluble compounds which can be easily removed, then the water left will be soft. It is on this principle the softening of hard water depends.

Removal of Temporary Hardness :

(*i*) *By boiling* : Temporary hardness of water can be removed simply by boiling the water, when the soluble bicarbonates are converted into insoluble carbonates which are precipitated.

$$Ca\,(HCO_3)_2 = CaCO_3 + H_2O + CO_2$$
$$Mg\,(HCO_3)_2 = MgCO_3 + H_2O + CO_2$$
$$Fe\,(HCO_3)_2 = FeCO_3 + H_2O + CO_2$$

The ferrous carbonate is however readily oxidised by air and then hydrolysed and precipitated as brown ferric hydroxide.

$$4FeCO_3 + 6H_2O + O_2 = 4Fe\,(OH)_3 + 4CO_2.$$

This method is effective on a domestic scale only and is too expensive for softening on a large scale.

(ii) By clerke's process : By this process temporary hard water is softened for industrial purposes by the addition of calculated quantity of slaked lime to water. Ca $(HCO_3)_2$ is precipitated as $CaCO_3$. while, if Mg $(HCO_3)_2$ be present, double the amount of lime is added when sparingly soluble Mg $(OH)_2$ is formed.

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 = 2CaCO_3 + Mg(OH)_2 + 2H_2O.$$

If too much slaked lime is added, free Ca^{++} ions enter the water by solution of the lime, and the water again becomes hard. Hence it is necessary to avoid addition of excess lime.

Removal of Permanent Hardness :—This kind of hardness cannot be removed either by boiling or by clarke's process. Permanently hard water is softened by the addition of sodium carbonate. The Ca^{++} and Mg^{++} ions are precipitated as insoluble carbonates by double decomposition :

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$
$$MgCl_2 + Na_2CO_3 = MgCO_3 + 2NaCl.$$

However, on a large scale, both the temporary and parmanent hardness are removed by any one of the following processes :

(a) Lime-soda process,
(c) Calgon process,
(b) Permutit process,
(d) Ion-exchange process.

(a) Lime-Soda Proecss :—In this process a mixture of slaked lime and sodium carbonate (soda) is added to hard water, which is warmed and stirred. This alkali mixture really contains Ca $(OH)_2$, Na_2CO_3 and NaOH, for a partial hydrolysis of soda takes place as follows :

$$Ca(OH)_2 + Na_2CO_3 \rightleftharpoons CaCO_3 + 2NaOH$$

These substances precititate the soluble salts of calcium, magnesium and iron, as carbonats or hydroxides and the water becomes soft.

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 = 2CaCO_3 + Mg(OH)_2 + 2H_2O$$
$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$
$$MgCl_2 + 2NaOH = Mg(OH)_2 + 2NaCl$$

etc. etc.

The precipitate is allowed to settle and then removed by filtration.

(b) *Permutit process* :—This is the most convenient and effcetive method used now-a-days for softening both temporary and permanent hard water. The permutit is the trade name for atificially prepared sodium aluminium silicate which is obtained by heating together sand, sada and china clay. This permutit resembles the naturally occuring mineral, Zeolite which has an approximate composition, $NaAl(SiO_3)_4, 2H_2O$. For convenience we may express permit or Zeolite as Na_2Ze. When permutit is placed in water containing soluble calcium or magnesium salt, the sodium of permutit is exchanged by calcium or magnesium and sodium passes into solution. Hence, this process is also called '*Base-exchange procees*'.

In the permutit process a wide vertical tower is packed with granules of permutit placed between two layers of gravel. Hard water is allowed to percolate down the column of permutit (Fig 19·1), when its sodium ions are replaced by calcium and magnesium ions present in the water and the very cause of hardness is removed. The issuing water, free form calcium and magnesium salts, is soft.

$$Na_2Ze + CaCl_2 = CaZe + 2NaCl$$
$$Na_2Ze + MgSO_4 = MgZe + Na_2SO_4$$

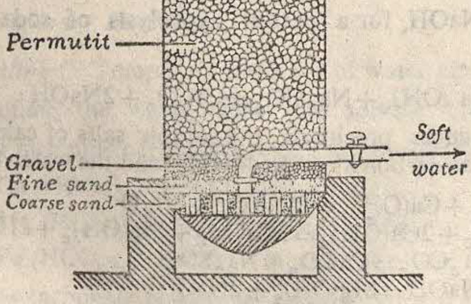


Fig. 19.1 : Permentit process

When the operation is carried out for several days, the permutit loses its sodium entirely and is exhausted. Then a concentrated brine (NaCl) Solution is run down through the column instead of water. In this process sodium ions replace the calcium and magnesium ions from the 'spent up' permutit bed so that it is regenerated and ready for use again.

$$CaZe+2NaCl=CaCl_2+Na_2Ze$$
$$MgZe+2NaCl=MgCl_2+Na_2Ze$$

The same permutit can thus be used for a long time for softening hard water. Permutit water-softening plants are used on a small scale in private houses, and also on a large scale for softening the public water supplies of towns.

(c) *Calgon Process* :—Many forms of sodium phosphate are used in softening hard water, but the most important among them is sodium hexameta-phosphate, $Na_2\ [Na_4(PO_3)_6]$, commercially called calgon. On treatment with hard water. sodium hexameta phosphate forms non-ionisable and highly soluble, stable complex anions with calcium, magnesium and iron and thus prevents their interaction with soaps. Hence the water is softened.

$$Na_2[Na_4(PO_3)_6]+CaSO_4=Na_2[Na_2Ca(PO_3)_6]+Na_2SO_4.$$

(d) **Softening by ion exchange resins : Demineralisation of water** :—In the different softening processes mentioned above, the undesirable Ca, Mg, Fe-ions are removed and these are replaced by equivalent amounts of other ions—notably Na^+ ions. Hence the water, though soft, is not ion-free. Practically ion-free water can be produced by treatment of water with some special synthetic resins. There are two types of synthetic ion-exchange resins :

(i) *Cation exchange resins* : These contain hydrogen which they exchange with cations present in water. Hydrogen passes into water as H^+ ions. The cation exchangers (represented by HR) are generally sulphonated organic compounds of high molecular weights like Zeocarb H.

(ii) *Anion exchange resins* : These contain hydroxy groups which they exchange with anions present in water. The anions are thus replaced by OH^-—ions. The anion exchangers (represented by R′OH) are hydroxy compounds derived from organic amines of high molecular weights, like Amberlite IRA – 400.

For softening, the raw water is allowed to percolate first through a tower packed with cation-exchange resins, when all the metal cations present in water are removed by exchange with hydrogen ions. The effluent water contains acids of the anions of the intake water, e.g , HCl, H_2SO_4, CO_2 etc. If 'HR' denotes such a resin, then

$$2HR+Ca(HCO_3)_2=CaR_2+2H_2O+2CO_2$$
$$2HR+MgSO_4=MgR_2+H_2SO_4$$
$$HR+NaCl=NaR+HCl \quad \text{etc.}$$

The CO_2 formed in the reaction may by driven out by blowing air through the solution,

The acid water is next passed through a tower packed with anion-exchange resins, which remove the anions of the acids by exchange with OH^- ions. If R′OH denotes such a resin, then

$$R'OH+HCl=R'Cl+H_2O.$$
$$2R'OH+H_2SO_4=R'_2SO_4+2H_2O \text{ etc.}$$

The water finally coming out of the anion exchanger is very pure water practically free from all electrolytes (Fig 19 2.). Such water is called de-mineralised or de-ionised water and it is as good as distilled water for all practical purposes.

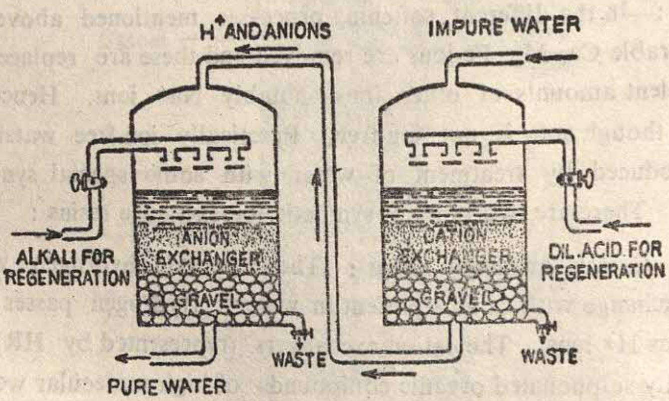


Fig 19.2. Soflcuing of water : Ion exchange process

When the ion-exchange resins become saturated with cations and anions, the original resins are revived by treating them with 0·2M H_2SO_4, (for cation exchangers) and 0·2M NaOH solution (for anion exchangers). The same resins are reproduced.

$$CaR_2 + H_2SO_4 = 2HR + CaSO_4$$
$$R'_2SO_4 + 2NaOH = 2R'OH + Na_2SO_4$$

Deionised water is soft and also free from other ions. It is very much used for medicinal and other analytical purposes. The distillation process of purification of water is better but involves much greater cost.

Many small size de-mineralisation apparatus are now available in the market and are suitable for domestic use.

19 5. Estimation of hardness of water : The hardness of water is expressed as 'degree of hardness', where 1 degree of hardness means the presence of 1 part by weight of $CaCO_3$ (or its equivalents) in 1,000,000 parts by weight of water.

Let us consider a simple of water 1 kg of which contanis ·024 gm of $MgSO_4$ in solution. Then 1,000,000 gm of water contains 24 gm. $MgSO_4$.

Now, 1 mol of $MgSO_4 = 1$ mol of $CaCO_3$.

or, 120 gm $MgSO_4 = 100$ gm $CaCO_3$.

$\therefore$ 24 gm of $MgSO_4 = \frac{100}{120} \times 24 = 20$ gm $CaCO_3$.

Hhnce the degree of hardness of water sample is 20°.

The degree of hardness of water is estimated by titrating a measured volume of water against a standard soap solution until a lather lasting for 2 minutes is otained on shaking—the soap solution is previously standerdised by titration against water containing a known concentration of calcium chloride. This gives a measure of total hardness of water. Temporary hardness is then removed by boiling the same volume of water and parmanent hardness is now estimated in the same way. The difference between the two results gives the temporary hardness of the given sample of water.

A modern method of estimating total hardness of water is to titrate it with a reagent called E. D. T. A. (ethylene diamine tetra-acctic acid) using some dyestuff as indicator.

19·6. Water used for different purposes : Natural water obtained from various sources must be treated in such a way so that it can be used for a particular purpose. Water is generally used.

(1) for industrial purposes ;
(2) for drinking purposes ;
(3) for chemical purposes ;
(4) for washing and other household purposes ;
(5) in irrigation and so on

1. **Industrial water** :—(a) *Boiler water*—Water to be used in boilers should be softened so to avoid the trouble of (i) Scale formation, (ii) Corrosion and (iii) Foaming. It the water is hard greater consumption of fuel will be needed and the life of the boiler will be shortened. Thus sea water etc. are not suitable for feeding boilers with. (b) *Water for Laundry*—Water to be used in laundries should be soft of nearly zero hardness (obtained by permutit process) to avoid extravagant use of soap. Laundry water must also be free from iron to avoid brown stains on fabrics.

(c) Water for chemical industries, such as paper, artificial silk, dyeing etc. must also be soft and particularly free from iron.

2. **Drinking water** :—The drinking water (portable water) should have a refreshing pleasant taste. Water need not be softened for drinking purposes ; the small quantities of dissolved salts and carbon dioxide improves its taste and also makes it beneficial for health. The drinking water should be hygienically safe. It must be free from pathogenic or disease-causing bacteria and hence should be sterilised. It should also be free from nitrogenous substances (ammonia or nitrates) and from salts of copper and lead. Drinking water must be to some extent hard, if it is coveyed through lead pipes, since soft water in presence of dissolved oxygen dissolves out lead as slightly soluble $Pb(OH)_2$, which is a cumulative poison. Chemically

pure water or distilled water (which is, infact very soft water) is tasteless and unsuitable for drinking purposes.

To provide drinking water to large population in cities or towns, river water is usually pumped into settling tanks. Here water is treated with lumps of alum which help to settle the suspended impurities at the bottom, precipitated aluminium hydroxide carries down suspended particles of clay, etc. and also some bacteria :

$$Al_2(SO_4)_3[\text{from alum}] + 3Ca(HCO_3)_2 = 3CaSO_4 + 2Al(OH)_3 + 6CO_2$$

The partly clarified water from the top then runs into big filter-beds having thick layers of fine sand, course sand and graded gravel. These layers remove the suspended impurities completely and also most of the bacteria. The bed is provided with drains below the gravel layer to carry off the filtered water which is pumped up into storage tanks. Before its supply to the consumers, the filtered water is sterilised either hy injecting adequate dose of chlorine or adding bleaching powder or somtimes by bubbling ozonised oxygen through the water. A short exposure to ultraviolet rays kills the bacteria without imparting any offensive smell or taste to the water.

On a smaller scale for domestic purpose, water is boiled to destroy the bacteria, and then treated with a little alum to coagulate the suspended matter. The water is next filtered through a suitable filter and used for drinking purposes.

3. **Pure Water** :—Chemically pure water is necessary in photography, in the preparation of medicines, in chemical analysis and for other chemical purposes. Water sufficiently pure for most chemical purposes in made by distilling water from a copper vessel fitted with a condenser of copper, tin, or silver, and collecting the middle portion of the distillate. It should be stored in steamed good glass (Jena or pyrex glass) bottles. Water thus purified is free from dissolved solids, except alkali dissolved from the glass, but it still contains dissolved gases, ammonia and carbon dioxide mainly. To obtain still purer water, ammonia is first removed by passing chlorine into the boiling distilled water for some time. The chlorine is then boiled out and the water is redistilled after the addition of a

strong solution of potassium permanganate and caustic potash in an all pyrex glass apparatus. This is very pure water and is called conductivity water.

Very pure water may be made by partially freezing distilled water and collecting the ice crystals. The soluble impurities remain in the unfrozen water.

19.7. Properties of Water :

Physical Properties : (1) Pure water is a transparent, colourless liquid with no taste or odour. It appears faintly blue when viewed in thickness (2) Under one atmosphere, it freezes at O°C and boils at 100°C—these two temperatures serve for standard points in thermometry. (3) The density of water at 4°C is highest and is accepted as 1 gram per c.c., this is used as the standard for expressing denstties of other substances. Above and below 4°C, the density of water is lower. Its density in the solid state (ice) is 0·92 and hence ice floats on water. (4) Pure water is almost a non-conductor of electricity due to its negligible ionization into hydrogen and hydroxyl ions, $H_2O \rightleftharpoons H^+ + OH^-$. (5) Water is a bad conductor of heat and has the highest specific heat of all solid and liquid substances. (6) Water is a very powerful solvent, particularly for the electrovalent compounds, acids, bases and salts. Water molecule is polar and its dielectric constant (81) is high, and therefore such compounds are highly dissociated in aqueous solution. (7) Water readily forms *crystal hydrates* of definite composition with many compounds, e.g., blue vitriol, $CuSO_4$, $5H_2O$, oxalic acid crystals $H_2C_2O_4$, $2H_2O$, glauber's salt, Na_2SO_4, $10H_2O$ etc. (8) Water is readily absorbed by quicklime, conc. sulphuric acid, P_2O_5, fused $CaCl_2$, silicagel, etc. These substances are called dehydrating or desiccating agents. In some cases, the absorption involves chemical reaction ; e.g. $P_2O_5 + 3H_2O = 2H_3PO_4$.

Chemical Properties : (1) Pure water reacts with various metals like Na, K, Ca, Fe, Al, Zn etc. and metal-amalgams at different temperatures producing hydrogen and the hydroxides (or oxides) of the metals concerned, this has already been discussed.

(2) Non-metals like carbon and sulphur react with water at high temperatures. Thus on passing steam on red hot carbon, a mixture of carbon-monoxide and hydrogen (water gas) is obtained.

$$C+H_2O=CO+H_2.$$

(3) Water dissolves many metallic oxides producing alkalis and non-metallic oxides producing acids. Thus—

$$Na_2O+H_2O=2NaOH \qquad N_2O_5+H_2O=2HNO_3$$

$$CaO+H_2O=Ca\ (OH)_2 \qquad SO_2+H_2O=H_2SO_3$$

(4) Many salts and other compounds react with water and undergo hydrolytic decomposition. Thus compounds like metallic nitrides, carbides, phosphides, hydrides etc., give metallic hydroxides on hydrolysis ; as

$$Ca_3N_2+6H_2O=3Ca\ (OH)_2+2NH_3$$

$$CaC_2+2H_2O=Ca\ (OH)_2+C_2H_2$$

$$Ca_3P_2+6H_2O=3Ca\ (OH)_2+2PH_3$$

$$CaH_2+2H_2O=Ca\ (OH)_2+2H_2$$

Similarly some metallic salts and certain organic eompounds are readily hydrolysed by water ; as

$$FeCl_3+3H_2O=Fe\ (OH)_3+3HCl$$

$$PCl_5+H_2O=POCl_3+2HCl$$

$$CH_3COCl+H_2O=CH_3COOH+HCl$$

$$CH_3COOC_2H_5+H_2O=CH_3COOH+C_2H_5OH$$

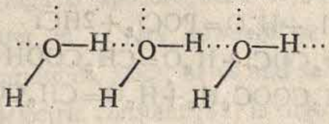
(5) Water is a stable exothermic compound ; $2H_2+O_2=2H_2O$ (steam) ; $\Delta H=-2\times 58000$ calories. It may be decomposed into its constituent elements on electrolysis or when heated to high temperatures (2000°C or above) in presence of tungsten or platinum (catalyst) or by electric sparks. Water is also decomposed by chlorine in presence of bright sunlight :

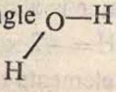
$$2H_2O+2Cl_2=4HCl+O_2$$

(6) Water appears to be a nceessany catalyst in many chemical and physical changes. Substances which react readily in normal conditions fail to do so if previously subjected to prolonged desiccation by exposure to phosphorus pentoxide. For example, sodium can be melted without reaction in dry chlorine ; dry carbon

monoxide and hydrogen do not burn in dry oxygen ; dry hydrogen chloride reacts neither with dry ammoina nor with dry calcium carbonate ; thermal dissociation of ammonium chloride is retarded by its prolonged drying.

19.8. **Anomalous properties of water :** water is the hydride of oqygen. If water is compared with the hydrides of neighbouring elements in the periodie table it will be found to exhibit many anomalous properties. For example, at room temperature water is a liquid, but H_2S is a gas though its molecular weight (34) is much large than that of H_2O (18). The boiling point of water is abnormally high. The density of a liquid normally increases with decreasing temperature and has the maximum value when it solidifies. The density of water, however, attains a maximum value at 4°C and ice is less dense than water. The specifie heat of water, and its latent heats of fusion and evaporation, are abnormally high, These anomalons behaviour of liquid water is explained by its tendency to undergo association. Water is an associated liquid—water molecules are joined by hydrogen bonding in ice and liquid water as shown below :



The water molecule is angular ; the bond angle  in water is 104°27', as a result the water molecnle is polar, its dipole moment is 1·84 Debye.

19.9 **Composition of water :** The composition af water can be determined by both *analytical* and *synthetic* methods.

Analytical method : Eletrolysis of water in a suitable voltameter is a ready means of showing that water is composed of two volumes of hydrogen and one volume of oxygen which are collceted at the cathote and at the anode respeetively.

Synthetic method : In this method the compostion of water may be determined both *volumetrically* as well as *gravimetrically*.

Volumetric composition : Though cavendish was the first to show that water is formed by the combination of two volumes of hydrogen and one volume of oxygen, his experiment is of historic interest only. The ratio by volume in which hydrogen and oxygen are combined in the formation of steam was established accurately by Hofmann.

Hofmann's Experiment : A U-shaped eudiometer tube is used in this experiment. One arm of the U-tube is closed and two platinum wires are fused at the top the closed limb, so that electric sparks may be produced inside when required. The closed limb is surrouded by a jaeket of a wider glass tube through which continually passed vapour of amyl alcohol boiling at 132°C. (Fig. 19·3.) A mixture of 2 volumes of hydrogen and 1 volume of oxygen is introduced into the closed limb of the U-tube by the displacement of mercury. When the gas mixture attains the steady temperature of 132°C its volume is noted by adjusting the ievels of mereury in the two limbs. The open limb is then closed firmly by the thumb, and an electric spark is passed in the gas mixture by connecting the platinum wires to an induction coil. An immediate contraction in the volume of the gas is observed, which is noted by adjusting the mercury levels in the two limbs as before after the gas attains steady temperature again. It is found that this volume is exactly two-thirds of the initial volume of the gas mixture. As the temperature is 132°C, any water formed is present as steam. The passage of amyl alcohol vapour is then cut off and the temperature of the closed limb is allowed to come down below 100°C. Mercury level slowly rises up and ultimately fills the closed limb completely. This is due to the fact that two-thirds of

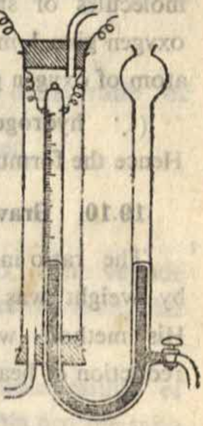


Fig. 19·3 Valumetric Composition of water the volume after explosion is entirely steam which condenses to liquid water of negligible volume. There is no uncombined hydrogen or oxygen left. It is thus established that 2 volumes of hydrogen combine with one volume of oxygen to give 2 volumes of steam.

Formula of Water :—The formula of steam may be dedued from the above observation as follows.—The result shows that, under the same condition of temperature and pressure.

2 volumes of hydrogen + 1 volume of oxygen yield 2 volumes of steam, and hence by avogadro's hypothesis :

2 molecules of hydrogen + 1 moleeule of oxygen yield 2 molecules of steam, or, 1 molecule of hydrogen + $\frac{1}{2}$ molecule of oxygen give 1 molecule of steam, i.e. 2 atoms of hydrogen + 1 atom of oxygen give 1 molecule of steam

($\because$ hydrogen and oxygen molecules are diatomic)

Hence the formula of steam (water) is H_2O.

19.10. Gravimetric Composition : Dumas Experiment :

The ratio in which hydrogen and oxygen are combined in water by weight was first accurately determined by Dumas in 1842. His method was based upon the formation of water by the reduction of heated copper oxide by means of pure hydrogen :

$$CuO + H_2 = Cu + H_2O.$$

Pure and dry hydrogen gas was passed over heated copper oxide of known weight kept in a vacuous bulb with a long neck (Fig. 19·4). Copper oxide was reduced to metallic copper. The water vapour produced was led by the current of hydrogen and was condensed in a previously weighed glass bulb and any uncondensed water

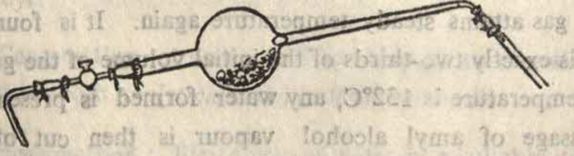


Fig. 19·4. Vacuous bulb used in Dumas Experiment vapour was absorbed in a series of U-tubes some containing solid caustic potash and others phosphorus pentoxide. After the experiment, the whole apparatus was cooled in a current of hydrogen—the hydrogen was then displaced by air. The increase in the weight of the bulb and the absorbing U-tubes gave the total weight of water formed, say x grams. The amount of oxygen say, y grams used up in the formation of water was obtained from the decrease in the weight of the copper oxide bulb. The quantity of hydrogen which took part in the production of water was obtained by subtracting the weight of oxygen from that of water, i.e. $(x-y)$ gms. It was found from Duma's experiment that the proportion by weight was $H : O = 1 : 7{\cdot}98$, which may be roughly taken to be equal to $1 : 8$, then

$$\frac{1}{8}=\frac{\text{a}\times\text{atomic weight of hydrogen}}{\text{b}\times\text{atomic weight of oxygen}},$$ where a/b is the ratio of atmos of hydrogen and oxygen in a molecule of water.

$$\therefore \quad \frac{1}{8}=\frac{\text{a}\times 1}{\text{b}\times 16}, \text{ whence } \frac{\text{a}}{\text{b}}=\frac{2}{1}.$$

Hence the molecular formula of water is H_2O. The vapour density of water has been found to be 9 and hence the molecular weight is 18 which supports the formula H_2O.

The most exact experiment on the gravimetric composition of water was carried out by Morley in 1895 who obtained the ratio of oxygen to hydrogen to be equal to 7.9396 to 1 by weight. This experiment has already been discussed.

19.11. Heavy Water : Heavy water or deuterium oxide D_2O is the oxide of heavy hydrogen, namely deuterium—the isotope of oridinary hydrogen. When water is electrolysed for a long time, the lighter isotope of hydrogen, i.e., ordinary hydrogen, is evolved preferentially, thereby causing a gradual enrichment of heavy hydrogen in the residual liquid in the electrolytic cell, which is gradually enriched in heavy water or D_2O molecules. By repeated distillation and electrolysis it has been possible to obtain nearly 99% pure heavy water.

Heavy water, like ordinary water, is a colourless liquid but it differs essentially in some physical properties from those of H_2O.

Property	H_2O	D_2O
(1) Mol. weight	18	20
(2) Density (20°c)	0·9982	1·1056
(3) Temp. of maximum density	4°C	11·6°C
(4) Freezing point	0°C	3 32°C
(4) Boiling point	100°C	101·4°C

Deuterium oxide resembles ordinary water in chemical properties. Among the chemical reactions of D_2O, the most important are the *exchange reactions*, in which H atoms in a compound are replaced by D atoms. Thus, $NH_3 \xrightarrow{D_2O} ND_3$; $HCl \xrightarrow{D_2O} DCl$; $CaC_2 \xrightarrow{D_2O} C_2D_2$ etc. D_2O reacts with sodium, evolving deuterium : $2D_2O + 2Na = 2NaOD + D_2$. Like water, it adds to salts forming deuterohydrates, e.g. $CuSO_4, 5\,D_2O$.

Heavy water is used (i) in atomic reactors as moderator for slowing down neutrons (ii) for studying the mechanism of chemical reations and (ii) for the preparation of heavy hydrogen.

Exercise—19

1. What are the common impurities which may be present in fresh water taken from natural source ? How do they affect the suitability of the water for domestic purposes ? How you would purity if (a) for industrial purposes and (b) for drinking purposes ?

2. (a) What observation would you make and what tests would you perfrom to establish a given liquid as water ?

   (b) How you would prepare a very pure sample of water ? Is such water suitable for drinking purposes ? Give reasons for your answer.

3. What is meant by hardness of water ? What is the hardness due to ? How can hardness be removed ? What are the disadvantages of hard water uses (a) in a laundry, (b) in a boiler ?

4. What is meant by "degree of hardness" ? How is it expressed ? A sample of water has 10° hardness. If the hardness is due to $MgCl_2$, how much $MgCl_2$ is present per kilogram of this sample of water ?

5. How and under what conditions does water react with (i) Calcium carbide, (ii) Aluminium nitride, (iii) Sodium peroxide (iv) Coke, (v) Phesphorus pentachloride, (vi) quicklime, (vii) Sodium, (viii) Iron, (ix) Calcium hydride.

6. Write notes on :

   (i) Calgon process, (ii) De-ionisation of water, (iii) Conductivity-water, (iv) Heavy water , (v) sterilisation of water (vi) Drinking water

7. (a) Oxygen and sulphur belong to the same group of the periodic table, but between their hydrogen compounds, water is liquid and hydrogen sulphide is gas. Explain this anomalous behaviour.

   (b) What is the difference between soft water and de-ionised water ?

8. Describe experiments for determinig the volumetric composition of Steam. How would you deduce its molecular formula ?

CHAPTER XX

OZONE

Molecular formula O_3 , Molecular weight 48, B. P. $-112°C$, weight of 1 litre 2·142 gm.

20·1 Allotropism :—Ozone and oxygen are two forms of the identical element. The molecules, however, possess different amount of chemical energy. Such different forms of a element are called allotropic forms or allotropes, and the phenomenon of an elementary substance appearing in more than one form is called allotropy or allotropism. Thus oxygen and ozone are allotropes. More striking examples of allotropy will be revealed in the study of phosphorus, Sulpher, carbon and tin. The allotropes of an element differ in their physical properties and also sometimes in their chemical properties. Allotropy generally results from the difference in the atomic arrangements in a crystal lattice or due to different types of molecules formed by the combination of atoms in more than one way. Oxygen and ozone provide example of the later type ; oxygen is diatomic, O_2 where as ozone is triatomic, O_3.

20·2. Ozone : occurrence.

Ozone is produced during the working of frictional electrical machines. Small quantities of ozone are produced when white phosphorus smoulders in air. There is a thin layer of ozone in the upper atmosphere. It is formed there by the action of ultraviolet rays of the sun on oxygen. This ozone layer in the atmosphere protcets us from the attack of the ultraviolet radiations. Electrolytically prepared oxygen at low temperature also contains some ozone.

20·3. Preparation : Laboratory method.

Mixed with oxygen, ozone (ozonised oxygen) is best prepared in the laboratory when pure and dry oxygen is submitted to a silent electric discharge—the oxygen is only partially converted to ozone. The change is endothermic : $3O_2 \rightleftharpoons 2O_3$; $\Delta H = +68{,}000$ cals. The electrical discharge dissociates some oxygen molecules into atoms, which then combine with other moleculs. At all temperatures, ozone is unstable and tends to revert to ordinary oxygen. The rate of reversion increases with rising temperature. Machines used for converting oxygen in air or in the pure state to ozone are known as ozonisers. Ozonisers make use of a silent discharge which is obtained by inserting some thin insulating materials, such as a glass plate or a mica sheet, in the gap through which the spark is passed. Heat generated by spark discharge would completely decompose ozone, and hence silent discharge is used. Temperature must be kept low during ozonisation. By cooling the ozoniser at O° and avoiding sparks the yield of ozone may be increased.

Two types of ozonisers are in general use :

1. **Siemen's Ozoniser :** The apparatus consists of two co-axial glass tubes. The outside of the outer and the inside of the inner tube are coated with sheets of tin foils. A current of dry oxygen is allowed to pass through the annular space between the two tubes (Fig. 20·1), the tin-foils are connected to the terminals of an induction coil. The oxygen is thus subjected to a silent electric discharge and the outcoming gas contains about 10% ozone—which turns starch-iodide paper blue.

2. **Brodies Ozoniser :** This apparatus consists of two vertical co-axial glass tubes (Fig 20.2). The inner tube, closed at the bottom, contains dilute sulphuric acid, and the whole arrangement

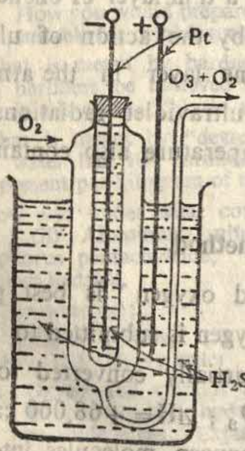


Fig. 20·2 Brodies ozoniser

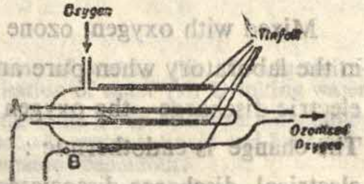


Fig 20·1. Simen's ozoniser

is partially inmersed in a jar of dilule H_2SO_4. The outer tube is bent in a U-shape for the exit of the gases. Two platinum wires connceted to the terminals of an induction coil, are dipped in the acid solutions inside and outside. Ozone is formed due to silent electric discharge when a slow stream of oxygen is passed through the annular space between the tubes. Ozonised oxygen, containing about 20% ozone, comes out through the exit tube.

Ozone may also be prepared by the electrolysis of ice-cold dilute sulphuric acid, using a high current density. The concentration of ozone in the gas liberated at the anode (a thin platinum wire) is about 14 per cent.

Pure Ozone is produced by the fractional distillation of the blue liquid obtaimed by cooling ozonised oxygen gas in liquid air. Liquid oxygen evaporats first, leaving behind less volatile blue liquid ozone, which on careful evaporation gives deep blue pure gaseous ozone.

20·4. Properties of Ozone :

Physical properties :—(1) Ozone is a bluish gas with a fishy smell. It may be condensed at −112°C to a dark blue explosive and highly magnetic liquid which freezes at −193°C to a dark purple solid. (2) It is slightly soluble in water (but more soluble than oxygen). It is **soluble** in organic solvents like carbon tetrachloride, glacial acetic acid, etc. It is readily absorbed by turpentine oil.

Chemical properties :—(i) Ozone decomposes slowly at ordinary tempratures and rapidly at 200°C into oxygen. Ozone is catalytically decomposed by finely divided substances, such as platinum black, silver oxide, manganese dioxide, powdered glass etc. $2O_3 \rightleftharpoons 3O_2$.

(ii) Ozone behaves as a very powerful oxidising agent. It is stronger oxidant and more reactive than oxygen.

(a) It oxidises lead sulphide to lead sulphate, ferrous salts to ferric salts, nitrites to nitrates and liberates iodine from acidified potassium iodide solution :

$$PbS + 4O_3 = PbSO_4 + 4O_2$$
$$2FeSO_4 + H_2SO_4 + O_3 = Fe_2(SO_4)_3 + H_2O + O_2$$
$$NaNO_2 + O_3 = NaNO_3 + O_2$$
$$2KI + 2HCl + O_3 = 2KCl + H_2O + O_2 + I_2$$

The libration of iodine from potassium iodide takes place also in a neutral solution, which then becomes alkaline,—

$$2KI+H_2O+O_3=2KOH+O_2+I_2.$$

In these reactions each molecule of ozone provides one atom of oxygen for oxidising the substance and it is itself reduced to a molecule of oxygen.

(b) If ozone takes part in oxidations which can be effected by molecular oxygen, the entire ozone molecule is absorbed. Thus it oxidises sulphur dioxide to sulphur trioxide, and stannous chloride to stannic chloride :

$$3SO_2+O_3=3SO_3\ ;\ 3SuCl_2+6HCl+O_3=3SuCl_4+3H_2O.$$

(c) Most metals, except gold and platinum, are oxidised by ozone at ordinary temprature. Mercury loses its mobility in contact with ozone, possibly due to the formation of an oxide which is soluble in the metal, and the mercury adheres to the glass. Ozone produces a layer of brown oxide on the surface of metallic silver :

$$2Hg+O_3=Hg_2O+O_2\ ;\ 2Ag+O_3=Ag_2O+O_2.$$

(d) Many non-metals are slowly oxidised in contact with ozone. Thus ozone oxidises moist sulphur, phosphorus and iodine into sulphuric, phosphoric and iodic acids.

$$S+H_2O+3O_3=H_2SO_4+3O_2$$
$$2P+3H_2O+5O_3=2H_3PO_4+5O_2$$
$$I_2+H_2O+5O_3=2HIO_3+5O_2$$

It liberats halogens from their hydracids :

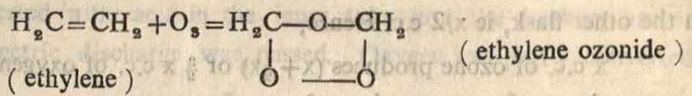
$$2HCl+O_3=Cl_2+H_2O+O_2.$$

(iii) Ozone also acts as a reducing agent in certain cases. Thus, when barium peroxide and hydrogen peroxide react with ozone, mutual reduction takes place, ozone itself being converted into oxygen.

$$BaO_2+O_3=BaO+2O_2\ ;\ H_2O_2+O_3=H_2O+2O_2.$$

Ozone does not react with potassium permanganate or potassium dichromate solution.

(iv) Ozone adds to unsaturated organic compounds e.g., ethylene, benzene and turpentine, to form ozonides :



$$\underset{\text{(ethylene)}}{H_2C=CH_2} + O_3 = \begin{array}{ccc} H_2C & —O— & CH_2 \\ | & & | \\ O & —— & O \end{array} \quad \text{(ethylene ozonide)}$$

Rubber loses its elasticity when kept in contact with ozone.

(v) Ozone acts as a bleaching agent. It bleaches vegetable colours by oxidation—indigo is bleached colourless by ozone.

20.5. Tests for Ozone :—The presence of ozone can be tested as follows :—(i) Besides its fishy smell, its action on mercury is distinctive—ozone 'tails' mercury.

(ii) Ozone responds to the general tests for oxidising agents, such as the liberation of iodine from potassium iodide—it turms starch-iodide paper blue.

(iii) Benzidine solution turns brown and alcoholic solution of tetramethyl base turns violet by the action of ozone.

20.6. Uses of Ozone :—(a) Ozone is a disinfectant : it is used for purifying the air in underground railway tunnels, in crowded halls and hospital chambers and for sterilising water. (b) Ozone is used for bleaching oils, waxes, ivory etc. (c) It is sometimes applied in analysis of unsaturated organic conpounds.

20.7. Formnla of Ozone :—Ozone is made from pure oxygen by silent electric discharye and it may be reconverted entirely into oxygen only by heat. The molecule of ozone, there fore, contains aloms of oxygen only. Formula of ozone was determined frist by Soret in 1866.

(a) *Soret's Experiment* :—Two similar flasks, with graduated necks, containing eqnal volumes of the same sample of ozonised oxygen, are inverted over water (Fig 20.3.). A tittle turpentine is admitted into one flask which immediately absorbs the ozone, producing a contraction of, say, x c.c. That is, the volume of ozone is x c.c.

The other flask is next heated long enough to ensure complete decompositon of ozone into oxygen. The flask is cooled to the original temperature and the gas is found to have expanded. The expansion is found to be exactly half the contraction which occurs in the other flask, ie x/2 c.c. Hence,

x c.c. of ozone produces $(x+\frac{1}{2}x)$ or $\frac{3}{2}$ x c.c. of oxygen.

or, 1 c.c. of ozone produces $\frac{3}{2}$ c.c. of oxygen.

By Avogadro's hypothesis, therefore.

n molecules of ozone produce $\frac{3}{2}n$ molecules of oxygen or 1 molecule of ozone produces $\frac{3}{2}$ molecules or 3 atoms of oxygen. Therefore, the molecular formula of ozone is O_3.

The formula of ozone was confirmed by Soret from its relative density, determined by comparing its rate of diffusion with that of chlorine. In one such experiment it was found that:

$$\frac{\text{relative rate of diffusion of chlorine}}{\text{relative rate of diffusion of ozone}}=\frac{0{\cdot}227}{0{\cdot}271}=0{\cdot}838\ .$$

Hence, by Graham's law of diffusion ;

$$\sqrt{\frac{\text{relative density ozone}}{\text{relative density of chlorine}}}={\cdot}0838\ .$$

Hence, relative density of ozone $=(0{\cdot}838)^2\times 35{\cdot}45=24{\cdot}9$

The molecular weight of ozone $=2\times$ relative density $=49{\cdot}8$.

This corresponds with the formula O_3. Vapour density of pure ozone, as determined by Duma's method was found to be 20·4, This confirms the formula O_3.

(*b*) *Newth's Experiment* : The apparatus shown in Fig. 20·4, similar to that of Brodie's ozoniser was devised by Newth to determine the volumetric composition of ozone. There were two co-axial detatchable tubes. The inner tube was closed at the bottom and contained dilute H_2SO_4 ; its upper end was broad and just fitted the outer wider tube. To the outer tube was attached a sulphuric acid manometer (mercury cannot be used as ozone tails mercury). In the annular space was placed a thin tube sealed at both ends containing turpentine, which remained clamped by glass projections from the walls of the tubes. The annular space was filled with pure oxygen and the whole arrangement was placed in a beaker containing ice-cold dilute sulphuric acid (not shown in the figure). Two platinum wires, connected with an induction coil, were inserted in the acid in the inner tube and the beaker, and a silent electric discharge was passed. Oxygen was partly converted

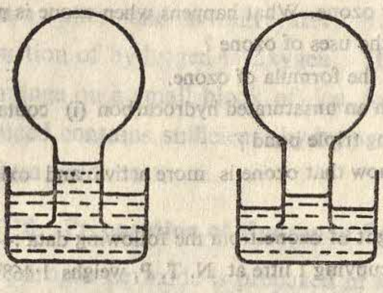


Fig 20·3 Sorets apparatus

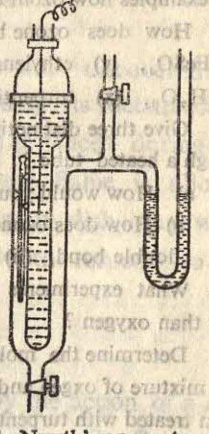


Fig. 20·4. Newth's apparatus

into ozone and the contraction (say v c.c.) was noted from the manometer. The turpentine tube was then broken by twisting the inner tube, all the ozone formed was absorbed, and a second contraction, equal to twice the first, was recorded by the manometer. Hence, the volume of ozone formed = 2 v cc.

and the volume of oxygen used up in ozonisation

= total contraction in volume = 3 v cc.

∴ 2 v cc. of ozone was formed from 3 v cc, oxygen,

or, 2 cc. of ozone was formed from 3 cc. of oxygen

∴ From Avogadro's hypothesis,

1 molecule of ozone was formed from $\frac{3}{2}$ moleculs or 3 atoms of oxygen.

Hence the molecular formula of ozon is O_3

It has been shown that the molecular structure of ozone is O=O The molecule is angular, the O—O—O angle being 116°49′.
↘
O

Exercise—20

1. Explain what is meant by the term allotropy. Name three elements which exhibit allotropy and mention their important allotropes. How do you know that Ozone is an allotrope of oxygen ?

2. Describe how oxygen can be ozonised, and illustrate with refrence to three examples how ozonised oxygen differ from ordinary oxygen.

3. How does ozone behave towards : (i) mercury, (ii) PbS, (iii) KI, (iv) $FeSO_4$, (v) ethylene, (vi) SO_2 gas, (vii) noist phosphorus, (viii) Ag, (ix) H_2O_2, (x) turpentive,

4, Give three distinctive tests for ozone. What happens when ozone is passed through a heated tube ? What are the uses of ozone ?

5. a) How would you establish the formula of ozone.

b) How does ozone react with an unsaturated hydrocarbon (i) containing double bond, (ii) containing triple bond ?

6. What experiments tend to show that ozone is more active and oxidising agent than oxygen ?

7. Determine the molecular weight of ozone from the following data :—

A mixture of oxgen and ozone occupying 1 litre at N. T. P, weighs 1·468 gms. When treated with turpentine, 50 c.c. only of the mixture are absorbed,

CHAPTER XXI

HYDROGEN PEROXIDE

Molecular fomula H_2O_2, Mol. wt. 34·016, Specific gravity 1·5, freezing Point—1·7°C.

21·1 **Occurrence** : Hydrogen peroxide was discovered by Thenard in 1818. There is uncertainty regarding its occurence in the atmosphere and in rain water. It is fomed in traces during the conbustion of hydrogen in oxygen. If a hydrogen flame is allowed to impinge on a small block of ice in a platinum dish, the water produced contains sufficient hydrogen peroxide to respond to the titanium oxide test.

21·2 Preparation of Hydrogen Peroxide :

Hydrogen peroxide is prepared in solution by the action of a cold dilute acid upon metallic peroxids containing the—O—O—group, such as barium peroxide and sodium peroxide.

Laboratory preparation ;—(1) Form barium peroxide,—Hydrogen peroxide is prepared by the action of cold dilute sulpheric acid on hydrated barium peroxide, $BaO_2, 8H_2O$.

$$BaO_2, 8H_2O + H_2SO_4 = BaSO_4 \downarrow + H_2O_2 + 8H_2O.$$

Finely ground barium peroxide is made into a paste of hydrated barium peroxide, $BaO_2, 8H_2O$, by slowly stirring with water and kept at a low temperature (0°C). The paste is used because anhydrous barium peroxide in not readily acted on by dil. H_2SO_4 due to the fomation of a coating of insoluble $BaSO_4$ on BaO_2 paiticles preventing further action. The paste of hydrated barium peroxide is then gradually added to ice-cold dilute H_2SO_4 acid with stirring, until the solution is just faintly acidic—a trace of acid acts as a stabiliser of hydrogen peroxide. Barium sulphate is precipitated. It is allowed to settle and then filtered off—the filtrate is an aqueons solution of 10 to 20% hydrogen peroxide.

In more recent practice, the hydrated barium peroxide is decomposed by phosphoric acid :

$$3BaO_2 + 2H_3PO_4 = Ba_3(PO_4)_2 + 3H_2O_2.$$

The precipitated barium phosphate is filtered off, leavning a solution of hydrogen peroxide, which is concentrated by distillation under reduced pressure. The product obtained by this method is of better stability, since phosphoric acid acts as a better preservative of hydrogen peroxide.

Aqueous solution of hydrogen peroxide can also be prepared by passing carbon dioxide into a suspension of finely powdered barium peroxide in ice-cold water. Barium carbonate is precipitated and filtered off and a solution of hydrogen peroxide is fromed :

$$BaO_2 + H_2O + CO_2 = BaCO_3 + H_2O_2$$

(*ii*) *From sodium peroxide*—When the calculated amount of sodium peroxide is slowly added to a saturated solution of sodium hydrogen phosphate cooled in icc, until the solution is just acidic, hydrogen peroxide is formed :

$$Na_2O_2 + 2NaH_2PO_4 = 2Na_2HPO_4 + H_2O_2.$$

Most of the disodium hydrogen phosphate separates on cooling as crystals of the hydrate, Na_2HPO_4, $12H_2O$ and is removed by filtration. A strong solution of hydrogen peroxide is thus obtained.

21·3 Industrial preparation :

(i) Merck's process :—In this process, calculated amount of sodium peroxide is added slowly to a 20 percent ice-cold dilute sulphuric acid solution, when hydrogen peroxide is fomed.

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2$$

On cooling, a large proportion of the sodium sulphate separates from the solution as the crystalline drcahydrate, Na_2SO_4, $10H_2O$, known as Glauber Salt and is filtered off. This removes much of the water. The filtrate is distilled in vacuo, when a 30%, H_2O_2 solution is obtained, which is known as 'perhydrol'.

(*ii*) *Electrolytic method* :—When more concentrated hydrogen peroxide is required for industrial purposes, it is prepared by electrolysing ice-cold 50% H_2SO_4, at high current densities using platinum electrodes. Sulphuric acid at this concentration is ionised as follows :

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

Hydrogen is liberated at cathode : $2H^+ + 2e = H_2$.

At the anode the HSO_4^- ions lose their charge, and associate to give perdisulphuric acid : $2HSO_4^- - 2e = H_2S_2O_8$.
Thus hydrogen is produced at the cathode and perdisulphuric acid, $H_2S_2O_8$ at the anode. The perdisulphuric acid undergoes hydrolysis when the solution remaining at the end of the electrolysis is distilled under reduced pressure, thus

$$H_2S_2O_8 + 2H_2O = 2H_2SO_4 + H_2O_2$$

and a solution of hydrogen peroxide is obtained as the distillate. Approximately 30% H_2O_2 can be obtained in this way. Such solutions when distiled under reduced pressure reaches a concentration of about 90% which is fainly stable in presence of suitable inhibitors like glycerol or phosphoric acid.

21·4. Preparation of Pure (anhydrous) hydrogen peroxide :

Hydrogen peroxide is separated from water by making use of its lower volatility (B. pt. of water 100°C, of hydrogen peroxide 151°C). When a dilute solution of H_2O_2 is allowed to evaporate in an open dish at 70°C, the concentration of H_2O_2 can be increased to 60 percent,—further evaporation leads to its decomposition into water and oxygen. By successive distillations under reduced pressure (85°C/66 mm), hydrogen peroxide of nearly 99% purity can be obtained. (Fig. 21·1) If the 99% solution of hydrogen peroxide is cooled to

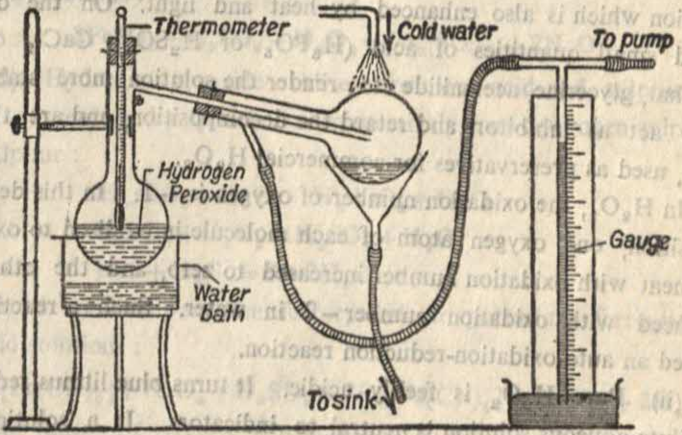


Fig. 21·1. Concentration of H_2O_2 solution under reduced pressure.

$-10°C$, and seeded with a crystal of solid hydrogen peroxide made by cooling a portion of the solution with solid carbon dioxide, pure crystals of hydrogen peroxide are obtained.

21·5. Properties of Hydrogen Peroxide :

Physical properties : Pure hydrogen peroxide is a syrupy, transparent liquid, colourless seen in small quantities, but blue in bulk. It smells like nitric acide and is miscible with water, ether and alcohol. Its specific gravity is 1·46 at 0°C and freezes at $-0{\cdot}89°C$. It decomposes explosively at its boiling point (151°C under normal atm. pressure), but may be safely distilled under reduced pressure (the B. Pt. at 68 mm. pressure is 84°C).

Chemical properties : (i) Hydrogen peroxide is rather unstable, it is more stable in aqueous solution than in anhydrous condition. It readily breaks out to yield water and oxygen evolving much heat, $2H_2O_2=2H_2O+O_2$; $\Delta H=-46120$ calories. Decomposition is promoted by the presence of finely divided substances, such as, colloidal Au and Pt, MnO_2, dust particles, charcoal powder and in contact with rough surfaces. Alkalis (OH^-) accelerate the decompostion which is also enhanced by heat and light. On the other hand small quantities of acid (H_3PO_5 or H_2SO_4), $CaCl_2$ or of alcohal, glycerine, acetanilide etc., render the solution more stable—they act as inhibitors and retard the decomposition, and are therefore, used as preservatives for commercial H_2O_2.

In H_2O_2, the oxidation number of oxygen is -1. In this decompossition, one oxygen atom of each molecule in oxidised to oxygen element with oxidation number increased to zero, and the other is reduced with oxidation number -2 in water. Such a reaction is called an auto-oxidation-reduction reaction.

(ii) Pure H_2O_2 is feebly acidic. It turns blue litmus red, but a dilute aqueous solution is neutral to indicators. If a solution of sodium carbonate is added drop by drop to a concentrated solution of hydrogen peroxide, sodium peroxide is formed with the evolution of carbondioxide.

$$Na_2CO_3+H_2O_2=Na_2O_2+H_2O+CO_2.$$

If, however, the carbonate is in excess, oxygen is evolved by the catalytic decomposition of hydrogen peroxide. The reaction of hydrogen peroxide with barium hydroxide solution is also typical of the acid-base reaction :

$$H_2O_2+Ba(OH)_2=BaO_2+2H_2O.$$

(iii) *Oxidising action of hydrogen peroxide* : Hydrogen peroxide is a powerful oxidising agent. (a) It oxidises black lead sulphide to white lead sulphate ;

$$PbS+4H_2O_2=PbSO_4+4H_2O.$$

use is made of this reaction in restoring the colour of old oil-paintings which is turnished due to the action of atmospheric hydrogen sulphide upon the white lead pigment.

(b) It liberates iodine quantitatively from acidified potassium iodide solution ;—a reaction used for the estimation of hydrogen peroxide :

$$2KI+H_2O_2+2HCl=2KCl+I_2+2H_2O.$$

(c) Ferrous salts are oxidised of ferric salts by hydrogen peroxide in acid solutions :

$$2FeSO_4+H_2SO_4+H_2O_2=Fe_2(SO_4)_3+2H_2O.$$

(d) Hydrogen peroxide oxidises arsenious acid and sulphurous acid to arsenic and sulphuric acid respectively, and hydrogen sulphide to sulphur :

$$H_3AsO_3+H_2O_2=H_3AsO_4+H_2O.$$
$$H_2SO_3+H_2O_2=H_2SO_4+H_2O.$$
$$H_2S+H_2O_2=S+2H_2O.$$

(e) It oxidises potassium ferrocyanide to potassium ferricyanide in acid solutions :

$$2K_4[Fe(CN)_6]+H_2O_4+H_2SO_4=2K_3[Fe(CN)_6]+K_2SO_4+2H_2O.$$

One atom of oxygen is provided by each molecule of H_2O_2 for oxidation purpose. H_2O_2 is reduced to water when its acts as an oxidising agent.

(iv) *Reducing action of hydrogn peroxide* : H_2O_2 also acts as a reducing agent towards powerful oxidising agents.

(a) It reduces potassium permanganate (pink in colour) in acid solution quantitatively to manganese sulphate—pink colour is discharged :

$$2KMnO_4+3H_2SO_4+5H_2O_2=K_2SO_4+2MnSO_4+8H_2O+5O_2.$$

(b) Hydrogen peroxide reduces silver oxide to metallic silver, ozone to oxygen, chlorine to hydrogen chloride, lead dioxide to lead monoxide. Solutions of bleaching powder and sodium hypobromide liberate oxygen on reduction :

$$Ag_2O+H_2O_2=2Ag+H_2O+O_2$$
$$O_3+H_2O_2=H_2O+2O_2$$
$$Cl_2+H_2O_2=2HCl+O_2$$
$$PbO_2+H_2O_2=PbO+H_2O+O_2$$
$$NaOBr+H_2O_2=NaBr+H_2O+O_2$$
$$Ca(OCl)Cl+H_2O_2=CaCl_2+H_2O+O_2$$

(bleaching powder)

(c) An alkaline solution of potassium ferricyanide is reduced to ferrocyanide by hydrogen peroxide :

$$2K_2Fe(CN)_6+2KOH+H_2O_2=2K_4Fe(CN)_6+2H_2O+O_2.$$

In the above reactions, a molecule of H_2O_2 first decomposes giving an atom of oxygen which then combines with an atom of oxygen of the substance with which it is reacting, to produce a molecule of oxygen. Thus oxygen is evolved in those reactions where H_2O_2 acts as a reducing agent.

(v) *Formation of addition compounds* : Hydrogen peroxide forms addition compounds with some salts like sodium sulphate, ammonium sulphate, sodium borate, potassium fluoride etc., in which it corresponds to water of crystallisation ; they are known as perhydrates. Examples are,—Na_2SO_4, $9H_2O$, H_2O_2 $(NH_4)_2SO_4$, H_2O_2 ; $NaBO_2$, $3H_2O$, H_2O_2 ; KF, H_2O_2.

(vi) *Bleaching Property* : Hydrogen peroxide has bleaching properties. It bleaches delicate fabrics, straw, silk, feather etc. Old paintings are often restored to their original tint by treatment with dilute H_2O_2 solution. In fact, H_2O_2 releases oxygen ($H_2O_2 \rightarrow H_2O+O$) which bleaches by oxidation.

21·6. Tests for Hydrogen Peroxide : (1) Hydrogen peroxide turns starch-iodide paper blue due to the liberation of iodine by H_2O_2 (even in the presence of ferrous sulphate).

(2) Hydrogen peroxide turns titanium dioxide in acid solution orange due to the formation of titanium trioxide : $TiO_2 + H_2O_2 \rightarrow TiO_3 + H_2O$. The test is highly sensitive.

(3) H_2O_2 decolourises the pink colour of the acidified potassium permanganate solution.

(4) An acidified $K_2Cr_2O_7$ solution when added to dilute H_2O_2 solution, produces perchromic acid. The mixture is rapidly shaken with ether, the ether layer at the top turns blue confirming the presence of perchromic acid. This is a delicate test for H_2O_2.

$$K_2Cr_2O_7 + H_2SO_4 + H_2O = K_2SO_4 + 2H_2CrO_4$$

$$H_2CrO_4 + 2H_2O_2 = CrO_5 + 3H_2O.$$

21·7. Strength of H_2O_2 solution : The strength of hydrogen peroxide solution is generally expressed in 'volume strength', i.e., it is sold in the market as "10 vol. hydrogen peroxide", "20 vol. H_2O_2", "30 volume H_2O_2", etc. A "10 volume H_2O_2" means that 1 cc. of this sample would give 10 cc. oxygen at N. T. P. on decomposition by heat or by contact with a catalyst. Other volume strengths are similarly defined.

(a) It is easy to convert the 'volume strength' into percentage strength of the solution and vice-versa.

We know $2H_2O_2 \longrightarrow 2H_2O + O_2$

(68 gms.) 22400 cc. at N.T.P.

∴ 1 gm. $H_2O_2 \equiv 22400/68 \equiv 329{\cdot}4$ cc. O_2

Suppose we have 1% H_2O_2 solution, then 100 cc. of 1% solution ≡ 1 gm $H_2O_2 \equiv 329{\cdot}4$ cc. O_2.

∴ 1 cc. of 1% $H_2O_2 \equiv 3{\cdot}294$ cc. O_2.

Hence the volume strength of 1% $H_2O_2 \equiv 3{\cdot}294$ vols.

i.e. 3·294 vol H_2O_2 solution ≡ 1% H_2O_2 solution.

or, x-vol H_2O_2 Solution $= x/3{\cdot}294\% \equiv 0{\cdot}3035x\%$.

Hence 20 vol H_2O_2 solution ≡ 20x0·3035·3035 = 6·07% H_2O_2.

and 10% H_2O_2 solution $= 10 \times 3{\cdot}294 = 32{\cdot}94$ vol H_2O_2.

(b) To find out the volume strength of 1(N) H_2O_2 solution :—

1(N) H_2O_2 solution contains 17 gms of H_2O_2 per litre.

[∵ equivalent weight of $H_2O_2 = 17$]

∴ 1(N) H_2O_2 solution $= 1{\cdot}7\%$ H_2O_2 solution

$= 1{\cdot}7 \times 3{\cdot}294$ vol H_2O_2 solution

i, e 5·6 vol H_2O_2.

21·8. Uses of hydrogen Peroxide : H_2O_2 is used—

(a) as an oxidising agent in the laboratory,

(b) as a bleaching agent for delicate materials like silk, ivory-works, paintings, hair etc.

(c) as an antichlor to remove excess of chlorine from bleached fabrics.

(d) as an antiseptic in dressing wounds, as a mouth wash, gargle, etc.

(e) as an oxidant for rocket ,fuels in concentrated (85%) form.

21·9 Composition and formula of hydrogen peroxide :

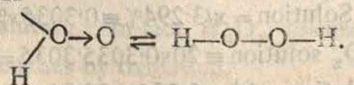
Hydrogen peroxide contains hydrogen and oxygen only, on decomposition it produces water and oxygen. Thenard found that 34 parts by weight of hydrogen peroxide yield 16 parts by weight of oxygen and 18 parts by weight of water. Again 18 parts by weight of water contain 16 parts by weight of oxygen and 2 parts by weight of hydrogen. Hence 34 parts by weight of hydrogen peroxide contain 2 parts by weight of hydrogen and $(16+16)=32$ parts by weight of oxygen. Consequently the ratio of the atoms of hydrogen and oxygen in hydrogen peroxide is $\frac{2}{1} : \frac{32}{16}$ i,e. 1 : 1. Hence the formula of hydrogen peroxide is $(HO)_n$.

Now, the vapour density of hydrogen peroxide under reduced pressure at 90°C is 17 ; its molecular weight, is therefore, 34.

∴ $(HO)_n = 34$ or $17 \times n = 34$ ∴ $n = 2$.

The formula of hydrogen peroxide is, therefore, H_2O_2.

It is probable that hydrogen peroxide is a mixture of two forms in dynamic equilibrium.



21·10 Hydrogen Peroxide and Ozone :

There are certain similarities between hydrogen peroxide and ozone, (i) Both of them are powerful oxidising agents, viz, both can liberate Iodine from potassium iodide and oxidies PbS to $PbSO_4$.

(it) Both of them possess some reducing properties, viz., H_2O_2 reduces Ag_2O, ozone reduces BaO_2.

(iii) Both possess bleaching properties : Ozone bleaches indigo, where as H_2O_2 bleaches delicate fabrics.

(iv) Both of them are unstable and give oxygen on decomposition.

However, there are certain distinguishing features between these two substances. These are tabulated below :—

Properties	**Ozone**	**Hydrogen peroxide**
1. Physical state etc.	i) Allotrope of of oxygen, Deep blue gas with fishy smell. ii) an endothermic compound	i) A peroxide, pale blue syrupy liqiuid smells like nitric acid. ii) an exothermic Compound.
2. Reaction to litmus	Neutral	Faintly acidic.
3. Solubility	i) very slightly soluble in water, ii) Soluble in CCl_4 and terpentine	i) miscible with water ii) Soluble in ether.
4. Chemical reaction—		
a) $KMnO_4 + H_2SO_4$	no reaction	Pink colour discharged.
b) $TiO_2 + H_2SO_4$	no reaction	orange colour developed.
c) Treated with mercury	mercury loses mobility	No action
d) Ag_2O	no change	Reauced to metallic Ag.
e) $KI + FeSO_4$ solution	no change	iodine liberated
f) $K_2Cr_2O_7 + H_2SO_4 +$ ether	no change	ethereal layer turns blue
g) alcoholic sols of tetramethyl base	violet colour	no change of colour

Exercise—21

1. a) How would you prepare a dilute solution of hydrogen peroxide in a laboratary ? why hydrated barium peroxide is used ? By what tests the presence of hydrogen peroxide can be confirmed ?

2. Describe the principle in preparing hydrogen peroxide by electrolytic method. What procedure would be nessary in order to obtain the compound in the pure state ? What are the important uses of hydrogen peroxide ?

3. Hydrogen peroxide behaves both as an oxidising agent and as a reducing agent—Discuss.

4. Describe, giving equations and condition, the action of hydrogen peroxide on :

a) lead sulphide, b) ozone, c) chlorine, d) silver oxide, e) acidified potassium permanganate solution, f) potassium iodide, g) colloidal platinum h) ferrous sulphate acified with sulphuric acid.

5. What is 'Merck's perhydrol' ? How is its prepared ? What is meant by '30 volumes hydrogen peroxide' ?

6. How the strength of hydrogen peroxide solutions is generally expressed ? How is the volume strength of H_2O_2 solution converted into percent strengh ?

7. a) What is the precentage strength of 100 vols H_2O_2 ?

b) What is the 'vol-strength' of a 2N H_2O_2 solution ?

c) How much lead sulphide shall be oxidised by 0.32 moles of H_2O_2 ? (Pb = 208, S = 32)

d) 10 ml. of a given solution of H_2O_2 gave 22.4 ml. of oxygen (measured at N. T. P.) when heated with colloidal platinum. How many grams of hydrogen peroxide were there per litre of the solution ?

[Ans. a) 30·4% b) 11.2 vols H_2O_2, c) 19·2 gms, d) 6·8 gms]

8. Make a comparative stuty of ozone and hydrogen peroxide.

CHAPTER XXII

THE ATMOSPHERE : NITROGEN

The term atmosphere is applied to the gaseous envelop that surrounds the earth and in which we live, this is commonly called *air*. In ancient times, air was considered an element by the early Greek alchemists. During the latter half of the eighteenth century, Priestley, Scheele, Lovoisier and Cavandish showed experimentally that air was principally a mixture of two gases, oxygen and nitrogen approximately in the proportion of one to four by volume. In addition to these gases, air contians small quantities of carbon-dioxide, water vapour and inert gases like helium, neon, argon etc. Traces of sulphur dioxide, nitric and nitrous acid vapours, ammonia and ozone are also present in air.

Since air is a mixture of different gases, its composition varies from place to place and from time to time. Usually 1·4% water vapour (by volume) is present in air which can be removed by passing air over fused calcium chloride. The approximate average composition of dry air is as follows :—

Component	Percent by volume	Percent by weight
Nitrogen	78·09	75·53
Oxygen	20·94	23·14
Inert gases	0·94	1·30
Carbondioxide	0·03	0·03

22·1 Constituents of Air, their detections and functions :—

(1) Oxygen and Nitrogen : (a) The presence of these two gases in air was established from the famous experiment of Lavoisier (1775). Lavoisier took some mercury in a retort the neck of which was bent so as to enter into a bell-jar containing measured volumeof air over mercury (Fig22. 1). The retort was then heated in a furnace to a temperature near the boiling point of mercury when the mercury in the retort changed

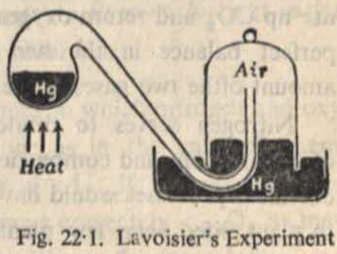


Fig. 22·1. Lavoisier's Experiment

into a red substance and the level of mercury in the bell-jar gradually rose up showing that a portion of air in the bell jar was being used up in the process. Eventually it was found that only one fifth of the air in the bell jar was used up and the residual gas was not absorbed by mercury, would not support the burning of a candle when introduced, nor would it allow respiration of a mouse. This remaining gas was named *nitrogen.*

Lavoisier next performed the reverse experiment. He collected the red substance from the retort and heated it strongly, when a gas came out. The volume of the gas obtained was found to be the same as was previously used up from the air. This gas strongly supported the combustion of a burning candle, and was named *oxygen.* Thus Lavoiseir concluded that air is composed of two gases, one supports life and combustion called oxygen and the other is a non-supporter of life and combustion called nitrogen, approximately in the ratio of 1 : 4 by volume.

(b) The presence of oxygen can be easily demonstrated by exposing a jar of nitric oxide to the air. Reddish brown fumes are produced showing that air contains free oxygen. The presence of nitrogen can be easily detected in the residual gas, left after the removal of oxygen by burning phosphorus, moist iron filings, heated copper turnings, etc., in a clored volume of air. This residual gas can be absorbed by heated magnasium, hence it is nitrogen.

Oxygen supports combustion and respiration, and is essential for the existance of life on this planet. Without oxygen in the atmosphere, the living kingdom would disappear. Animals take up oxygen from air and return carbondioxide to the atmosphere ; while plants use up CO_2 and return oxygen to the atmosphere. There is, thus, a perfect balance in the two processes so as to maintain a constant amount ofthe two gases in the atmosphere.

Nitrogen serves to dilute the oxygen of air and regulate the rate of respiration and combustion within our bodies. Otherwise the chemical processes would have been too rapid. Although essential to plant life, very few plants can assimilate it in the free condition. It is an extremely inactive element under ordinary conditions.

(2) **Carbon dioxide** : When clear lime water, taken in a watch glass, is exposed to air, a white scum is formed on its surface very soon and gradually the lime water turns milky. This is due to the formation of insoluble calcium carbonate as a result of the absorbtion of carbondioxide of the air by lime water. This proves the existance of CO_2 in air.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

Carbondioxide forms the chief food meterial for plants.

(3) **Water-vapour** : (a) Fine drops of water are found to be deposited on the onter surface of a glass containing ice inside. The moisture of the air in the immediate vicinity cools and deposits itself on the walls of the glass. This shows the presence of water vapour in air.

(b) The deliquescence of fused calcium chloride when kept exposed to air, the formation of dew, fog, mist, cloud etc. also show the existance of water vapour in the air.

Water vapour by alternate formation of clouds and rains supports plant and animal life. It also controls the evaporating power of the atmosphere.

22·2. Air is a mixture and not a compound : Air is a mixture of gases, mainly of nitrogen and oxygen, it is not a compound. This is evident from the following facts.

(1) The proportion of oxygen and nitrogen (also of other constituents) in air is not constant. There is a slight variation in different places and at different altitudes. If air was a compound its composition would have been constant. Even such slight variation in composition would not have been observed.

(2) The proportion (by volume) in which nitrogen and oxygen are found in the air is not a simple one, as in the case of chemical combinations. It is approximately 4 : 1. If air was a compound its formula would be N_4O or move correctcly $N_{15}O_4$ as may be deduced from the percentage composition. So its relative density

should be 36 or 137 respectively. But its actual density found experimentally is 14·4, which corresponds to a mixture of nearly 4 volumes of nitrogen and 1 volume of oxygen thus :

$100 \times d = 80 \times 14 + 20 \times 16, \quad \therefore \quad d = 14{\cdot}4$, where d = density of air (H = 1).

(3) There is no thermal change nor is there any volume change when nitrogen and oxygen are mixed together in the proportions they are present in air and the mixture behaves like ordinary air, while when gases combine chemically, there is always a thermal change, and often a change in volume. Thus air is not a compound.

(4) The air dissolved in water has the oxygen : nitrogen ratio 1 : 2, but in atmosphere the ratio is 1 : 4. This change in composition is due to the fact that air is a mixture and oxygen is more soluble in water than nitrogen. A compound would never change its composition in passing into solution.

(5) When air is allowed to diffuse though a porous partition, nitrogen, being lighter than oxygen, passes out more rapidly than oxygen, causing a partial separation of the constituents of air. Had air been a chemical compound, the constituents could not be seperated in this way—it would diffuse as a whole.

(6) On fractional distillation of liquid air, nitrogen evaporates off earlier than oxygen and the components can be separated. Distillation of a compound does not permit such separation of components, a compound distils as a whole.

22.3. Volumetric Composition of Air

(*a*) *Lavoisiers Experiments*—The volumetric composition of air may be determined by the classical experiments of Lavoisier on calcination of metals in air, which has been already described. (See sec. 22·1.) From his experiments, Lavoisier concluded that : (1) air is a mixture of two gases, nitrogen and oxygen, in the approximate ratio of 4 : 1 by volume. (ii) oxygen of air alone supports combustion and respiration.

(*b*) *Eudiometric method*—A known volume of dry air free from carbondioxide is taken in the closed limb of a graduated U-shapped eudiometer tube containing mercurry (Fig 22.2). Two platinum wires are fused at the end of the closed arm and there is a stop-cock attached to the bottom of the other arm. The volume (V_1 cc.) of the enclosed air is measured under external atmospheric pressure by adjusting the level of mercury in the two limbs to same height. Nearly equal volume of dry hydrogen is then introduced and the volume (V_2 cc.) of the mixture of air and hydrogen is determined as before. Then an electirc spark is passed through the gas mixture by connecting the pt-wires to the terminals of an induction coil. The whole of oxygen in air combines with hydrogen to from steam, which is condensed to liquid water on cooling occupying negligible volume. As a result, there is a contraction of the volume. At the same temperateme and pressere, the volume of the residual gas (V_3 cc.) is also read from the graduation. Hence,

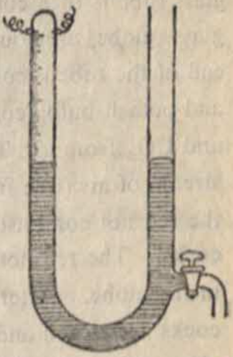


Fig. 22·2 Volumetric composition of air

The contraction in volume due to formation of water $=(V_2-V_3)$ cc.
Now, in water, the ratio of $H_2 : O_2 = 2 : 1$ by volume, hence one-third of this contraction is the volume of oxygen originally present in air.

∴ V_1 cc. of air contained $\frac{1}{3}(V_2-V_3)$ cc. of oxygen.

∴ Volume percent of oxygen in air $=\dfrac{100(V_2-V_3)}{3V_1}$.

The volume has experimentally been found to be approximately 21% oxygen. Thus air contains roughly 21% of oxygen and 79% of nitrogen by volume.

22.4. Gravimetric Compostion of air :

Dumas Experiment—The proportion of oxygen and nitrogen in air can be determined gravimetrically by Dumas method. In this method a long hard-glass combustion tube, fitted with a stop-cock at each end, is taken Fig (22·3). It is packed with pure copper turnings, evacuated and carefully weighed. This hard glass tube is then connected at one end with an empty (evacnated) glass globe, previously weighed and closed by a stop-cock. The other end of the tube is connected with U-tubes containing anhydrous $CaCl_2$ and potash bulb (containing KOH solution) for removing moisture and CO_2 from air. The tube is then strongly heated in a furnace and a stream of air (free from moisture and CO_2) is slowly passed through the red hot combustion tube into the glass globe by opening the stop-cocks. The red hot copper removes the oxygen and nitrogen collects tn the globe. After sometime, the supply of air is stopped, the stop-cocks are closed and the apparatus is allowed to cool. The hard glass tube and the globe are separately weighed. Some nitrogen remains in the tube, the tube is evacuated and again weighed. From these weights, the amount of oxygen and nitrogen in air can be obtained

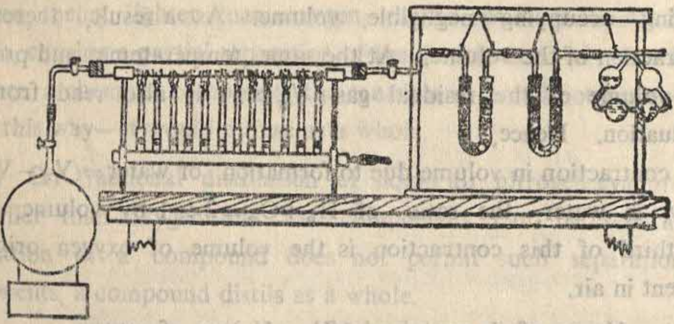


Fig 22.3. Gravimetric Composition of air.

Calculation—Suppose,

the weight of the evacuated globe $= w_1$ gm.

the weight of evacuated hard glass tube + copper $= w_2$ gm.

the weight of the globe + nitrogen after the experiment $= w_3$ gm.

the weight of hard glass tube + copper + CuO + Nitrogen present in it $= w_4$ gm.

the weight of hard glass tube + Copper + CuO (after evacuating nitrogen) $= w_5$ gm.

$\therefore$ weight of oxygen $= (w_5 - w_2)$ gm.

and weight of nitrogen = weight of nitrogen in the globe + weight of nitrogen in the hard glass tube.

$$= (w_3 - w_1) + (w_4 - w_5) \text{ gm.}$$

$\therefore$ Total weight of air $= (w_5 - w_2) + (w_3 - w_1) + (w_4 - w_5)$ gm.

$$= (w_3 - w_2 - w_1 + w_4) \text{ gm.}$$

$\therefore$ % of oxygen $= 100(w_5 - w_2)/(w_3 - w_2 - w_1 + w_4)$

and % of nitrogen $= 100\ [(w_3 - w_1) + (w_4 - w_5)]/(w_3 - w_2 - w_1 + w_4)$

If the experiment carefully conducted, the percentage composition of air will be found to be

oxygen = 22.92 parts by weight

Nitrogen = 77.08 parts by weight.

22.5. Estimation of water vapour and carbondioxide in air.

The amount of water vapour and carbondioxide in air may be estimated by passing a known volume of air though previously weighed U-tubes containing fused calcium chloride to absorb moisture, and then through weighed tubes containing solid KOH to absorb carbondioxide. The gain in the weight of calcium chloride U-tubes gives the weight of water vapour and that of potash tubes gives the weight of carbondioxide, present in air.

Carbondioxide is genrnlly estimated by shaking a known volume of air with standard baryta solution, and then titrating the excess of baryta left with a standard oxalic acid solution, using phenolphthalein as indicator.

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$

22.6 Liquid Air : It has already been discussed how air can be liquefied by using high pressere and very low temperature obtained by Joule-Thomson expansion. Liquid air is actually a mixture of liquid nitrogen and liquid oxygen, and it is a clear liquid with a pale-blue colour. It boils at −190°C. Liquid air is kept in donble-walled Dewar flasks, the space between the two walls being highly evacuated. The outer surface of the inner wall and the inner surface of the outer wall are silvered to minimise heat-flow. Many substance, like rubber, flowers, vegetables, meat etc, become hard and brittle when exposed to liquid air, metallic mercury becomes a malleable solid, lead and tin become elastics and zinc becomes very brittle.

Liquid air is mainly used for the industrial preparation of oxygen, nitrogen and inert gases by fractional distillation. It is also used for liquefying other gases and in research laboratories for attaining very low temperatures.

22.7. Inert Gases :—In 1895, the famous English scientist, Lord Rayleigh, observed that nitrogen made by removing all other gases from the air is denser than pure nitrogen made by decomposing ammonium nitrite, NH_4NO_2. This led to the suspicion that small amount of heavier gases might be present in the nitrogen obtained from air. Rayleigh and Ramsay passed the nitrogen obtained from the air over hot magnesium. Nitrogen was removed as magnesium nitride (Mg_3N_2) but a small amount of residnal gas was left which could not combine with any other element. This residual gas gave a new spectrum and was called argon (meaning idle or inert), as the gas was found to be chemically very inactive.

Subsequently, Ramsay and Travers discovered as many as five such inactive gases in air including argon, in extremely small amounts. These gases are helium, neon, argon, krypton and xenon. As these gases are present in minute amounts in air and are difficult to isolate, they are often called "Rare Gases". These are also known as "Inert gases or Noble gases", because they do not exhibit any tendency to undergo chemical change. Their chemical inertness leads us to believe that they have stable electronic configurations, i. e., the outermost shell of the atom is completely filled up in each case. Only xenon has been recently found to form a few compounds, like $XePtF_6$; XeF_4 ; etc.

These inert elements are all monatomic gases with very low boiling points, and belong to Zero Group in the Periodic Table. Their percentages in air are :

	He	Ne	A	Kr	Xe
% by volume	5×10^{-8}	$1{\cdot}5\times10^{-3}$	0·94	$1{\cdot}1\times10^{-4}$	9×10^{-6}

Of these, helium, neon and argon have commercial uses. Argon is extensively used in incandescent light bulbs to increase the intensity of the light and to prolong the life of the filament. Neon is used in most of the fluorescent advertising tubes often mixed with mercury vapour for different colours. Helium gas is extremely light—next to hydrogen and is non-inflammable and is therefore the ideal gas for filling ballooms.

NITROGEN

Atomic number 7, Atomic weight 14·008, Molecular formula N_2, Electronic Corfiguration $1s^2 2s^2 2p^3$, Boiling point $-195{\cdot}8$°C, melting point $-209{\cdot}8$°C, Normal density 1·2505 gm/lit.

22.8. Histroy and occurrence :—Nitrogen was recognised as a distinct substance by the scotch botanist, D. Rutherford in 1772, but its true nature was discovered by Lavoisier who called it azote meaning lifeless. Later the name nitrogen was suggested from the occurrence of the element in the familiar substance nitre.

Nitrogen occurs in the free state in air constituting about 78% of the atmosphere by volume. It is also abundant in the combined state. In combination, it is found in ammonia, nitre or potassium nitrate and chili saltpetre or sodium nitrate. It is a constant and essential constituent of all living matter, plant and animal, in the form of complex compounds called proteins.

22.9. Preparation of Nitrogen :—Nitrogen may be prepared either from air or from compounds containing nitrogen, such as ammonium compounds.

(a) **Form Air** :—Nitrogen may be obtained from air by simply removing the more reactive gases. Carbondioxide and watervapour are first removed by bubbling air through strong caustic potash solution and concentrated sulphuric acid in succession. Oxygen is then removed from the dry and purified air by the fallowing methods :

(*i*) *by red-hot Copper* :—When dry air is passed through a long tube containing red-hot copper turnings, the oxygen is removed as copper oxide and free nitrogen is obtained, the gas is collected over water ; $2Cu + O_2 = 2CuO$.

(*ii*) *by means of phosphorus* :—A porcelain crucible containing a piece of white phosphorus is allowed to float on water in a trough and covered with a graduated and stoppered bell jar, (Fig 22·4.). The phosphorus is then ignited by means of a hot wire and the stopper is closed. Phosphorus burns in the oxygen of the enclosed air giving off white fumes of phosphorus pentoxide which dissolves in water. $4P + 5O_2 = 2P_2O_5$. water gradually rises up in the bell-jar and fills one-fifth of the volume occupied by air. The remaining four-fifths are filled with the residual gas, which is mainly nitrogen. (iii) Oxygen may also be removed from air (at room temperature) by bubbling purified and dry air through an alkaline solution of pyrogallic acid, which absorbs oxygen and nitrogen gas is set free, which is collected over water.

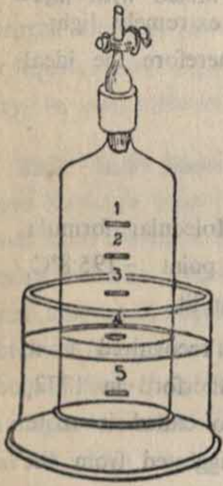


Fig. 22·4. Preparation of nitrogen from air

(iv) On the industrial scale nitrogen is prepared *by the fractional distillation of liquid air*. Air freed from carbondioxide and moisture is liquefied (See chap. xvii)..The liquid air is then fractionally distilled when more volatile nitrogen escapes first. Nitrogen is thus separated from oxygen and collected almost in the pure state.

N. B. It is to be noted that nitrogen obtained from air by removing oxygen is not pure. It is contaminated with the inert gases of the atmosphere like argon, neon, etc, as all direct methods for isolating nitrogen from air fail to remore these gases. Nitrogen so prepared contains about $1\frac{1}{4}$ percent of argon and other noble gases and its density is therefore slightly greater than that of pure nitrogen which can only be obtained from the compounds of nitrogen.

(b) From Compounds containing nitrogen :—

(i) *Laboratory method* :—Nitrogen is produced in the laboratory by heating ammonium nitrite.

$$NH_4NO_2 = N_2 + 2H_2O.$$

But direct heating of ammonium nitrite may sometimes occur with explosive violence. So nitrogen is usually propared by warming a concentrated solution of the equimolecular mixture of sodium nitrite and ammonium chloride when ammonium nitrite is first formed by double decomposition, which gives nitrogen on heating :

$$NH_4Cl + NaNO_2 = NaCl + NH_4NO_2$$
$$NH_4NO_2 = N_2 + 2H_2O.$$

The concentrated solution of equimolecular proportions of sodium nitrite and ammonium chloride is taken in a round bottom flask provided with a thistle funnel and a delivery tube. The end of the thistle funnel dips into the solution. The other end of the delivery tube enters into water taken in a pneumatic trongh over which a gas jar filled mith water is kept inverted (Fis 22·5). The flask is then slowly heated when nitrogen gas is evolved which passes through the delivery tube and is collected in the gas-jar by the displacement of water. The gas may be purified by passing over red-hot copper turnings and then through U-tubes containing concentrated KOH solution and concentrated sulphuric acid in succession. The pure and dry gas is then collected over mercury.

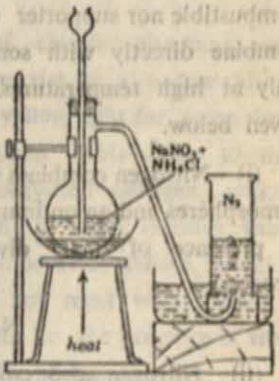


Fig. 22·5. Preparation of nitrogen

(ii) Pure nitrogen gas can also be obtained by heating ammonium dichromate or adding a suspension of bleaching powder to ammonia solution :

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2$$
$$3Ca(OCl)Cl + 2NH_3 = 3CaCl_2 + 3H_2O + 2N_2.$$

(iii) Ammonia may be oxidised to nitrogen by bubling chlorine gas through strong ammonia solution. Ammonia must be in large excess otherwise an explosive oily liquid, nitrogen trichloride, NCl_3, is produced.

$$3Cl_2+8NH_3=N_2+6NH_4Cl\ ;\quad 3Cl_2+NH_3=NCl_3+3HCl.$$

(iv) Pure nitrogen is obtained by heating barium azide or sodium azide ;

$$Ba(N_3)_2=Ba+3N_2\ ;\quad 2NaN_3=2Na+3N_2.$$

22·10. Properties of Nitrogen : Nitrogen is a colourless, tasteless and odourless gas, which is slightly soluble in water. Liquid nitrogen is colourless. In the gaseous state elementary nitrogen is diatomic. Nitrogen is more or less chemically inert. It is neither combustible nor supporter of combustion. However, nitrogen can combine directly with some elements, both metals and nonmetals, only at high temperatures. Some of its important reactions are given below.

(i) Nitrogen combines with hydrogen at a high pressure of 200 atmospheres and an optimum temperature of 550°C to from ammonia in presence of finely divided iron acting as a catalyst (Haber's process).

$$N_2+3H_2=2NH_3.$$

(ii) Nitrogen also combines with oxygen when the mixture of two gases is passed through an electric arc, and produces nitric oxide (Birkland-Eyde process).

$$N_2+O_2=2NO.$$

(iii) Nitrogen combines directly with metals like lithium, magnesium, calcium, barium and aluminium when heated to from nitride.

$$3Ca+N_2=Ca_3N_2\ ;\ 3Mg+N_2=Mg_3N_2$$

These nitrides, on hydrolysis with water or steam, give the corresponding metallic hydroxide and ammonia.

$$AlN+3H_2O=Al(OH)_3+NH_3.$$

$$Mg_3N_2+6H_2O=3Mg(OH)_2+2NH_3$$

(iv) Calcium carbide, on being heated in nitrogen at 1100°C combines with it to form calcium cyanamide, $CaCN_2$ and carbon. The mixture is called *nitrolim* and is very much used as a fertiliser.

$$CaC_2+N_2=CaNCN+C.$$

Calcium cyanamide is also easily hydrolysed to give ammonia when heated with water.

$$CaNCN+3H_2O=CaCO_3+2NH_3.$$

22 11. Uses : The main use of nitrogen is in the production of ammonia, nitrolim, nitric acid and nitrides. It is also sometimes used to furnish inert atmosphere in electric light bulbs and in mercury thermometres registering high temperature. Liquid nitrogen is used as a refrigerating agent.

22 12. Active Nitrogen : Action of electric dischange on nitrogen gas at low pressure (<1 mm) gives rise to a yellow after-glow, i.e, the gas continues to emit a yellow light for some time even after the discharge has been discontinued. This is due to the formation of a new modification of energy-rich nitrogen, which is called *active nitrogen.* 'Active nitrogen' is more reactive than ordinary nitrogen. It yields nitrides with vapours of sodium, arsenic, phosphorus, liquid mercury etc. which do not react with ordinary nitrogen. This enhanced reactivity is due to the presence of free atoms and energy rich molecules in the active nitrogen.

22 13. The Nitrogen Cycle : Nitrogen is essential for all living organisms, where it occurs in combination with carbon, hydrogen and oxygen mainly as proteins. It is essential that the living bodies should have abundant supply of nitrogen to synthesise their proteins in order to maintain the life processes. Air is a vast source of nitrogen, but it is inactive and with the exception of a few unicellular plants like *algae* and *fungi* and some bacteria, no animal or plant can assimilate gaseous nitrogen directly.

Animals get their supply of protein foods from the plants. Higher animals obtain protein from plants as well as from the meat, milk, etc. of the lower animals. Plants mostly take up nitrogen-supply from soil in the from of soluble nitrats (or nitrites) and ammonium salts. Only leguminous plants and some algae can utilise atmospheric nitrogen.

The ultimate source of nitrogen is thus the atmosphere. This nitrogen enters into life process of plants and animals through various processes and is again returned back as gaseous nitrogen in the air.

Consumption of atmospheric nitrogen takes place through the following processes :

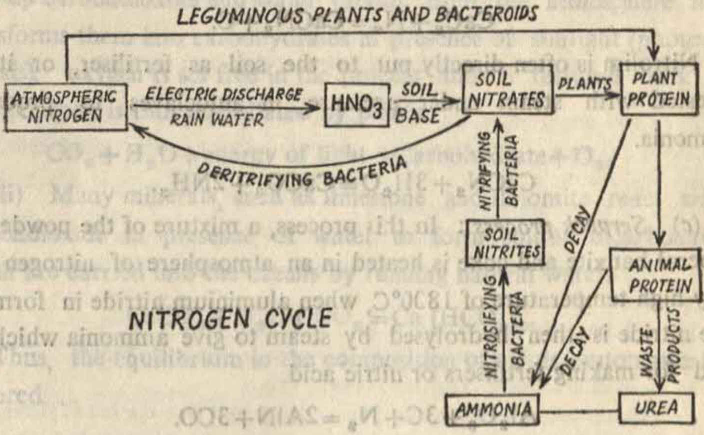
(i) During electric discharges in the upper atomsphere in lightning storms, nitrogen and oxygen combine to produce nitric oxide which is then oxidised by the excees of air into nitrogen dioxide and is washed down to the soil by rain as dilute nitric acid. The nitric acid is readily converted into soluble nitrates by the bases present there. The plants absorb the nitrates through their roots and finally transform them into proteins. Herbivorous animals acquire their necessary nitrogen by consuming the proteins of plants ; carnivorous animals by consuming the proteins in other animals.

(ii) Nitrogen is also withdrawn from air by certain leguminous plants, e.g., peas, beans, colver, etc. for their nutrition through the agency of symbiotic bacteria present in their roots.

Although the nitrogen is thus continuously removed from air, the nitrogen content of the atmosphere remains constant. This is due to the fact that there are reverse processes by which nitrogen is released in the gaseous form and returns back to the atmosphere. This takes place through the following processes :

When plants and animals die, the nitrogenous substances of their body suffer decay and putrefaction, giving rise to the formation of ammonia and liberation of some free nitrogen which goes back to the atmosphere. In a similar fashion, animal excretion plus waste products, for instance faeces and urine, lead to the production of a considerable quantity of ammonia and nitrogen. The ammonia, thus formed, is first converted in the soil to nitrites by the nitrosifying soil-bacteria and then to nitrates by the nitrifying soil-bacteria. These nitrates remain in the soil and partly supply nourishment to the plants and are partly transformed by denitrifying soil-bacteria to nitrogen which returns to the atmosphere.

Thus a continuous circulation of nitrogen is maintained in nature from atmosphere to plants, animals, soil and back again. The whole process is cyclic one and so harmoniously balanced that the nitrogen content of the atmosphere remains practically constant. This is called the *nitrogen cycle*. The cycle may be described by means of the following diagram.



22 14 Fixation of Atmospheric Nitrogen

The nitrogen cycle is not perfectly balanced from the standpoint of nutrition in modern ages, since considerable amount of nitrogen is lost to the sea by way of sewage and effluents from cities and thus becomes of no use to living beings. This loss is compensated now-a-days by the fixation of atmopherie nitrogen which means the conversion of a portion of the atmospheric nitrogen into useful nitrogenous compounds. We have seen that the nature itself has two ways of fixing the nitrogen. For increased demand, several artificial methods have now been developed to fix up the atmospheric nitrogen. The ontline of these methods are mentioned here.

(*a*) *Haber's process* : In this process, ammonia is obtained by dircet combination of hydrogen and nitrogen under high pressure of 200 atm. and at an optimum temperature of 550°C in presence of iron catalyst.

$$N_2 + 3H_2 = 2NH_3, \quad \Delta H = -23200 \text{ cal.}$$

This ammonia is converted into ammonium salts or urea, which are widely used as fertilizers.

(b) *Cyanamide process*: In this process nitrogen is passed over crushed calcium carbide heated to 1100°C in an elcetric furnace, when a greyish black mixture of calcium eyanamide and carbon is formed, which is called *Nitrolim*

$$CaC_2 + N_2 = CaCN_2 + C.$$

Nitrolim is often directly put to the soil as fertiliser, or it is digested with steam under pressure in autoclaves to produce ammonia.

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3.$$

(c) *Serpeck process*: In this process, a mixture of the powdered mineral bauxite and coke is heated in an atmosphere of nitrogen at very high temperature of 1800°C, when aluminium nitride in formed The nitride is then hydrolysed by steam to give ammonia which is used for making fertilisers or nitric acid.

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO.$$
$$2AlN + 3H_2O = Al_2O_3 + 2NH_3.$$

(d) *Birkland-Eyde process*: In this process air is passed through an elcetric arc at nearly 3000°C, when nitrogen and oxygen combine to give nitric oxide. This is then cooled and oxidised by air to NO_2. Subsequently it is converted into nitric acid by dissolving in water.

$$N_2 + O_2 = 2NO, \Delta H = +43200 \text{ cal.}$$

Of the above four processes, the methods (a) and (b) only are now technically important. Of the artificially fixed nitrogen, more than 80% go to the soil as fertiliser and the rest to production of explosives and other consumer goods. The overall balance of the nitrogen cycle is however maintained.

22 15. The carbondioxide Cycle : Due to the respiration of plants and animals, the combustion of fuels like, coal, wood, petroleum, etc, and the decay or decomposition of plants and animals, the proportion of carbondioxide in air gradually tends to increase with the consequent depletion of some oxygen of the atmosphere. But, the proportions of oxygen and CO_2 in air is maintained practically constant as a result of the simultaneous removal of carbondioxide in the following way ;

(i) chlorophyll, or the green colouring matter of the plants, taks up carbondioxide and water vapour from the atmosphere and transforms them into carbohydrates in presence of sunlight (photosynthesis). oxygen is set free in the process and is restored back to air. Carbon is thus assimilated by plants.

$$CO_2 + H_2O + \text{energy of light} \rightarrow \text{Carbohydrate} + O_2.$$

(ii) Many minerals, such as limestone and dolomite react with carbondioxide in presence of water to form soluble bicarbonates which are carried into the oceans by running natural water.

$$CaCO_3 + H_2O + CO_2 = Ca\,(HCO_3)_2.$$

Thus, the equilibrium in the composition of air is automatically restored.

Excercise—22

1. a) How would you prove that air and water contain a common constituent ? What are the evidences that in one case the common constituent is chemically conbined while in the other it merely forms part of a mixture ?

2. a) The formula of water is H_2O. Explain why no formula is given to air.

b) How can oxygen be a part of air and at the same time heavier than air ?

c) How is it that the atmosphere consists so largely of nitrogen, yet this element is not found so abundantly in the minerals of the earth's crust ?

3. Give an approximate composition of air. What experiments would you perform to show the presence of different components in air ? How carbondioxide and water vapour are removed from air ?

4. Describe a method for the determination of volumetric composition of air.

5. Describe Lavoisier's experiment on the composition of air. How is the composition of air affceted by plant and animal life ?

6. Write brief informative notes on :—

a) Rare gases of the atmosphere and their uses.

b) Liquid air.

c) Active nitrogen.

7. a) How is nitrogen prepared in the laboratory ? Mention some of its chemical reactivity.

b) Explain why nitrogen obtained from air is slighly heavier than nitrogen prepared from its compounds.

c) How would you proceed to prepare a sample of pure nitrogen ?

8. How can nitrogen be obtained from (a) air, (b) ammonia, (c) nitrc acid ? Under what conditions does nitrogen combine with (i) hydrogen, (ii) oxygen, (iii) magnesium and, (iv) calcium carbide ? Describe the action of water, if any on the products formed in each case.

9. What changes do you expect when the following substances are kept exposed to air ?

(i) white phosphorus, (ii) lime water, (iii) metallic sodium, (lv) sodium carbonate crystals, (v) anhydrous copper sulphate, (vl) quick lime, (vll) sodium hydroxide.

Give equations wherever necessary.

10. What is the 'nitrogen cycle' ? Explain why such a cycle is necessary.

11. Write briefly what is meant by fixation of atmospheric nitrogen and how the same is achieved.

12. Discuss, giving equations, what will happen when

a) ammonium nitrite and ammonium nitrate is separately heated

b) ammonia is passed over hot copper oxide,

c) calcium nitride and calcium cyanamide are kept in a current of steam,

d) magnesium ribbon is burnt in air and then the product is boiled with water,

e) nitric oxide is passed over heated copper,

f) ammonium dichromate is slowly heated,

g) chlorine gas is added to ammonia gas.

CHAPTER XXIII

COMPOUNDS OF NITROGEN

The atom of nitrogen has five valency electrons ; its compounds are formed by covalent linkages between the nitrogen and other atoms. Thus with hydrogen, nitrogen forms ammonia by sharing electrons with three hydrogen atoms, having the formula NH_3. Other hydrogen compounds of nitragen are Hydrazine N_2H_4 and Hydrazoic acid, N_3H. We shall describe the chemistry of ammonia in this chapter.

AMMONIA

[Mol. formula NH_3 ; Mol. weight 17, Normal Density 0·771 gm/lit.

23.1. Occurrence :—Ammonia is the most important of the hydrides of nitrogen. It is found in small quantities in the atmosphere. It is produced due to the putrefaction and slow decay of organic matter. The odour of ammonia is prevalent near stables and urinals, where such action goes on.

23·2. Preparation :

(a) **Laboratory Method** :—In the laboratory ammonia is prepared by heating an ammonium salt with a strong base like caustic soda or lime. Generally an intimate mixture of ammonium chloride and slaked lime in the proportion of 1 : 3 by weight, is heated in a round-bottom flask or a hard glass test tube fitted with a delivery tube (Fig 23·1.). Ammonia is evolved. The gas is dried by passing through a tower packed with quick lime (CaO) and then collected in gas jars by the down-ward displacement of air or over mercury.

$$2NH_4Cl+Ca(OH)_2=CaCl_2+2H_2O+2NH_3$$

Ammonia is best dried by means of qucik lime (CaO). Ammonia, being a basic substance, cannot be dried by conc. H_2SO_4 or P_2O_5 as these are acidic and would react with ammonia to form ammonium sulphate and ammonium phosphate respectively. It cannot be dried with fused $CaCl_2$, because calcium chloride absorbs the gas forming an addition-compound, $CaCl_2, 8NH_3$.

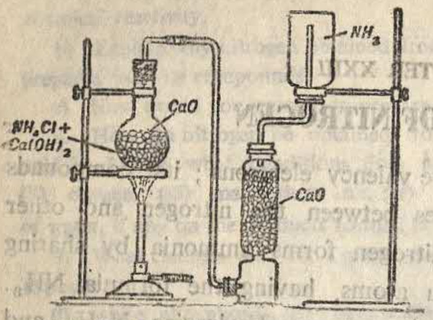


Fig. 23·1 Preparatton of ammonia

A continuous supply of ammonia gas can be readily obtained in the laboratory by dropping liquor ammonia from a dropping funnel into a flask containing solid caustic soda.

(b) Ammonia can also be obtained (i) by the reduction of nitrates (or nitrites) with zinc (aluminium or Devarda's alloy) and strong caustic soda solution :

$$NaNO_3+8H=NaOH+2H_2O+NH_3.$$

(ii) by the hydrolysis of some matallic nitrides and calcium cynamide.

$$2AlN+3H_2O=Al_2O_3+2NH_3$$
$$CaCN_2+3H_2O=CaCO_3+2NH_3$$

(iii) by the reduction of nitric oxide by hydrogen in presence of platinum catalyst.

$$2NO+5H_2=2NH_3+2H_2O$$

23·3. Properties of ammonia :

Physical Properties : Ammonia is a colourless gas with a very pungent smell. It is lighter than air and easily liquefied by cooling on compression (6 atmospheres at 10°C). Liquid ammonia boils at −33·4°C and processes remarkable solvent properties and dissolves many elements such as, sodium, potassium, calcium, iodine, phosphorus, etc. Ammonia is highly soluble in water. One c.c. of water can dissolve about 1200 cc. of the gas at 0°C. The concentrated

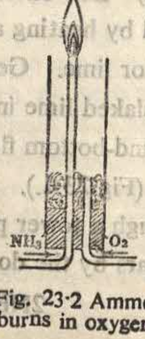


Fig. 23·2 Ammonia burns in oxygen

aqueous solution is called *liquor ammonia*. Gaseous ammonia readily escapes from the solution into the air and the whole of ammonia is expelled from the solution on boiling. A bottle of liquor ammonia should be carefully opened after cooling in ice, as there is always a high pressure inside.

Chemical Properties : (i) Ammonia itself is neither a supporter of combustion nor combustible. But it burns in oxygen with a greenish-yellow flame (Fig. 23 2).

$$4NH_3+3O_2=2N_2+6H_2O$$

Mixtures of ammonia with air or oxygen may be exploded by an electric spark, the products contains steam, nitrogen and oxides of nitrogen.

(ii) Although stable at ordinary temperatures, ammonia is largely decomposed into its elements by prolonged sparking ; at equilibrium the product contains 6 per cent. of ammonia, and 94 per cent of nitrogen and hydrogen.

$$2NH_3 \rightarrow N_2+3H_2$$

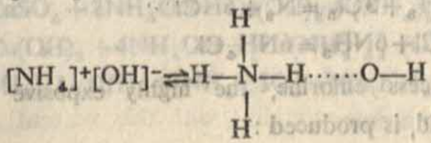
(iii) Ammonia is a weak base. It forms salts with acids,

$$NH_3+HCl=NH_4Cl \ ; \ 2NH_3+H_2SO_4=(NH_4)_2SO_4$$

(iv) Ammonia is very freely soluble in water as indicated before, and from this aqueous solution two solid hydrates, NH_3, H_2O and $2NH_3$, H_2O have been crystallised at low temrerature.

When dissolved in water, it forms ammonium hydroxide, NH_4OH, which is a weak alkali. Ammonium hydroxide turns red litmus blue, forms salts with acids, and dissociates to a small extent producing OH-ions, presumably due to hydrogen bonding which hinders dissociation of the base into ions.

$$NH_3+H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$



$$[NH_4]^+[OH]^- \rightleftharpoons \begin{array}{c} H \\ | \\ H—N—H\cdots\cdots O—H \\ | \\ H \end{array}$$

$$NH_4OH+HCl=NH_4Cl+H_2O.$$

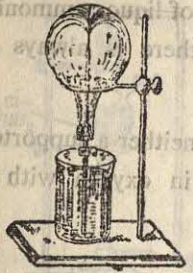


Fig. 23·3 Fountain experiment

The solubility of ammonia in water and the alkalinity of the solution can be easily showon by the "*fountain experiment*". A round bottomed flask is filled with dry ammonia gas and closed with a cork through which a narrow glass tube provided with a stop-cock is inserted (Fig. 23·3). One end of the tube which is inside the flask is drawn into a jet and the other end dips into a red litmus solution taken a beaker. The stop-clock is opened and the flask cooled by pouring a littl ether on its surface, which evaporates immediately. Due to cooling ammonia contracts and the red litmus solution rushes inside in the form of a fountain. As ammonia dissolves in the incoming aqueous solution, more and more liquid rush in and the colour of the liquid changes from red to blue. This experiment shows that ammonia is highly soluble in water and its aqueous solution is alkaline.

(v) Gaseous ammonia gives rise to typical compounds, amides, when passed over heated alkali metals. The amides are hydrolysed by water yielding ammonia back.

$$\underset{\text{(sodamide)}}{2Na+2NH_3=2NaNH_2+H_2} \; ; \; NaNH_2+H_2O=NaOH+NH_3.$$

(vi) Ammonia, in some cases acts as a mild reducing agent, when it is itself oxidised to nitrogen or nitric oxide. For example,

(a) When ammonia is passed over heated lead monoxide or copper oxide, it is oxidised to nitrogen and water.

$$2NH_3+3CuO=2Cu+N_2+3H_2O$$

(b) Ammonia reacts with chlorine to form, if ammonia is in excess, ammonium chloride and nitrogen :

$$2NH_3+3Cl_2=N_2+6HCl$$
$$6HCl+6NH_3=6NH_4Cl$$

whereas, with excess chlorine, the highly exposive nitrogen chloride, an oily liquid, is produced :

$$NH_3+3Cl_2=NCl_3+3HCl$$

(c) When a mixture of ammonia and air is passed over a platiunm gauze heated to 500°C the ammonia is smoothly oxidised to nitric oxide (Fig. 23·4)

$$4NH_4 + 5O_2 = 4NO + 6H_2O.$$

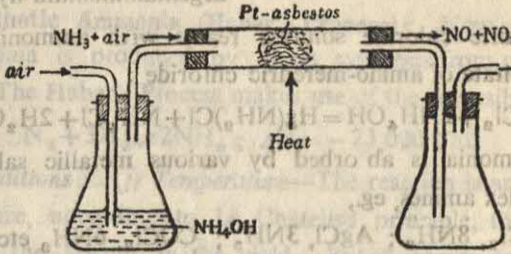


Fig. 23·4 Catalytic oxidation of ammonia

(vii) When 2 volumes of ammonia gas and 1 volume of carbondioxide are mixed, ammonium carbamate is produced.

$$2NH_3 + CO_2 \rightleftharpoons NH_2COONH_4.$$

(viii) Ammonium hydroxide (i,e eqeous solution of ammonia) can precipitate many metallic hydroxides from solutions of their salts.

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl$$
$$ZnSO_4 + 2NH_4OH = Zn(OH)_2 + (NH_4)\ SO_4,\ \text{etc.}$$

In some cases, the precepited metallic hydroxide (or oxide) redissolves in excess of ammonia solution owing to the formation of a cationic complex, for example

(a) When ammonia is added to copper sulphate solution, a pale blue precipitate of cupric hydroxide appears, which re-dissolves when more ammonia is added forming an intense blue solution, cantaining cuprammonium complexes.

$$CuSO_4 + 2NH_4OH = Cu(OH)_2 + (NH_4)_2SO_4.$$
$$Cu(OH)_2 + 4NH_4OH = [Cu(NH_3^{++})_4]\ (OH)_2 + 4H_2O$$
$$[Cu(NH_3)_4]\ (OH)_2 + (NH_4)_2SO_4 = [Cu(NH_3)_4]\ SO_4 + 2NH_4OH.$$

cuprammonium sulphate.

(b) Silver nitrate solution with NH_4OH gives a white precipitate of silver oxide (easily turning brown) with dissolves in excess of ammonia producing the complex argentammonium compounds.

$$2AgNO_3+2NH_4OH=Ag_2O+2NH_4NO_3+H_2O$$

$$Ag_2O+4NH_4OH=2[Ag(NH_3)_2]OH+3H_2O$$

argentammonium hydroxide

(ix)Mercuric chloride solution reacts with ammonia, giving a white precipitate of amino-mercuric chloride :

$$HgCl_2+2NH_4OH=Hg(NH_2)Cl+NH_4Cl+2H_2O.$$

(x) Ammonia is ab orbed by various metallic salts to form stable complex amines, eg.,

$CaCl_2, 8NH_3$; $AgCl, 3NH_3$; $COCl_2, 6NH_3$ etc.

23 4. Uses of Ammonia : (1) Considerable amount of ammonia is required for producing nitrogenous fertilisers, such as urea, ammonium sulphate, ammonium phosphate, etc.

(2) Ammonia is also employed for the manufacture of nitric acid (ostwald 'process), sodium carbonate and bi-carbonate (solvay process)•

(3) Liquid ammonia is used as a refrigerant in ice manufacture and also in refrigerators. Liquid ammonia is also used as fertiliser in some countries.

(4) Ammonia and some of its salts are used as laboratory reagents in chemical analysis.

235 Tests for Ammonia : Ammonia is recognised by the following properties : (i) it processes a characteristic pungent smell ; (ii) it turns moist red litmns blue and turmeric paper brown ; (iii) it produces a white cloud of ammonium chloride if brought into contact with geseous hydrogen chloride $NH_3+HCl=NH_4Cl$; (iv) it blackevs a filter paper moistened with mercurous nitrate solvtion ; (v) traces of ammonia or ammonium salts can be detected by Nessler's reagent. This reagent contains K_2HgI_4 in alkaline solution (obtained by dissolving HgI_2 in extess of KI solution and made alkaline with KOH solution), with this reagent ammonia produces a brown colour or a brown precipitate.

23 6. Manufacture of Ammonia : Ammonia is prepared on the industrial scale (1) by the direct combination of hydrogen and nitrogen (Haber's Process) ; (2) by the hydrolysis of calcium cyanamide ; and (3) as a by-product in the manufacture of coal gas and coke.

1. Synthetic Ammonia (Haber's Proeess) : Now-a-days most of the ammonia is produced by direct synthesis from nitrogen and hydrogen. The Haber's Process makes use of the reversible reaction.

$$N_2+3H_2 \rightleftharpoons 2NH_3 \ ; \ \Delta H = -23{,}000 \text{ Cal.}$$

(a) Conditions : (i) Temperature—The reaction is an exohermic one and hence, according to Le Chatelier principle, the lower the temperature the greater in the yield. But at low temperature the rate of reaction becomes slow and the process will not be economical. Hence the reaction is conducted at an optimum temperature of 550°C at which the speed of reaction is not too slow, nor the yield of ammonia is too low. In order to accelerate the reaction at this optimum temperature, a suitable catalyst is required. The catalyst is usually finely divided iron mixed with a promoter like molybdenum, or a mixture of alumina and potassium oxide.

(ii) Pressure : The reaction is accompanied with decrease in number of moles and hence in volume. Hence according to Le chatelier principle, the yield of ammonia will be large with higher

Percentage yield of ammonia (by volume)

Pressure / Temp	1	10	100	200	1000 atm
400°C	0·44	3 85	25·0	36 3	80·0
500°C	0·129	1,20	10·6	17·6	57·5
550°C	0·08	0·76	6·8	12·0	41·0
600°C	0·05	0·50	4·5	8 3	31·5

pressure—the yield being directly proportional to the applied pressure

Hence in this reaction higher pressures are always applied. The best workable condition has been found to be 200 atm. at the optimum temperature of 550°C. The table at page 111 shows how the proportion of ammonia in the equilibrium mixture depends on temperature and pressure.

(*b*) *Materials :* The source of nitrogen is air and that of hydrogen is steam. Air is passed over red-hot coke when producer gas ($CO+N_2$) is obtained. In a separate plant, steam is passed over red-hot coke. When water gas ($CO+H_2$) is produced. To a mixture of water gas and producer gas is added excess of steam and then passed over a contalyst of iron activated with alkali at 500°C. Carbonmonoxide is thereby oxidised to carbon dioxide :

$$CO+H_2O \rightleftharpoons CO_2+H_2$$

The carbondioxide is removed by absorption in water under pressure and the residual carbon monoxide, by ammoniacal cuprous chloride solution. The remaining gases (N_2 and H_2) are brought exactly to the ratio 1 : 3 by volume by addition of N_2 from Linde liquefaction plant and finally dried.

Method : The mixture of pure and dry nitrogen and hydrogen (1 : 3 by volume) is compressed to about 200 atmospheres and sent, by means of a pump, through a drying tower, into the catalyst chamber (Fig. 23·5), made of chrome-steel and containing the catalyst plus promoter in a central tube electrically heated to 550°C.

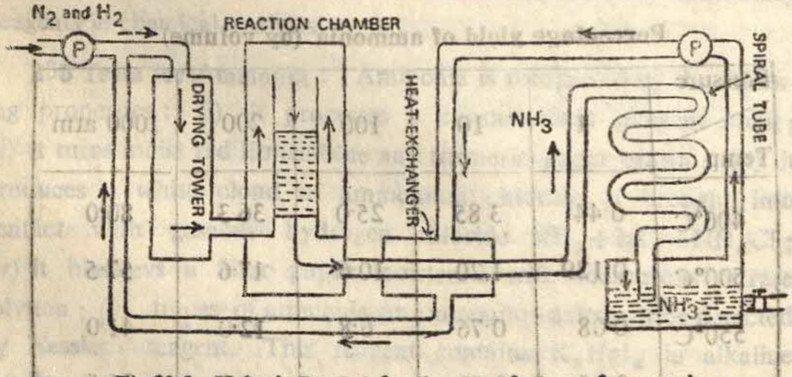


Fig 23.5 Haber's Process for the manufacture of ammonia

during the early stage of operation. The gases first circulate around the central hot tube and gets preheated. It then enters the catalyst chamber and in contact with the catalyst it produces about 12% of ammonia. Once the reaction starts external heating is unnecessary. The heat of reaction is sufficient to maintain the temperature of the catalyst. The issuing gases containing unreacted nitrogen, hydrogen, and ammonia (~ 12%) then pass through a heat-exchanger to preheat the unconverted nitrogen and hydrogen that are re-circulated, and are further cooled in a spiral tube. The ammonia formed is then absorbed, while still under pressure, in water in a reservoir producing a 25% solution of ammonia. Instead of dissolving ammonia in water, the gas may be condensed to a liquid by cooling due to Joule-Jhonson effect. The unreacted nitrogen and hydrogen are let out through a pipe and are re-circulated by another pump through the heat-exchanger and mixed with original reactant mixture, and the above process is continued. Argon, which unaviodably enters the plant with the nitrogen, is blown off from time to time.

The ammonia thus produced is largely used for making (a) ammonium sulphate, (b) urea and (c) nitric acid.

2. **Cyanamide process** : The process has been discussed in connection with the fixation of atmospheric nitrogen. This process is no longer followed for production of ammonia, but nitrolim, which is a product of this process, still manufactured for fertilisers.

3. **Ammonia from Gas-works** : Ammonia is obtained as a by-product in the manufacture of coal-gas. Coal contains about 1·0 ~ 1·4 percent of nitrogen and also some hydrogen. During the manufacture of coal-gas by the destructive distillation of coal, the nitrogen and hydrogen contained in the coal are transformed into ammonia and ammonium salts which are collected in the ammoniacal liquor as an aqueous solution. The ammoniacal liquor is separated and heated with steam when free ammonia comes out ; subsequently the residual liquor is treated with milk of lime and steam to obtain the

ammonia present as ammonium salts. The ammonia thus liberted, is sometimes dissolved in water to produce liquor ammonia or often absorbed in sulphuric acid to get ammonium sulphate which is used as a fertiliser. Each ton of coal yields about 12 kg. of ammonium sulphate.

23·7 Composition of Ammonia : Ammonia must contain only nitrogen and hydrogen as it can be synthesised directly from these two elements. The volumetric composition of ammonia and its molecular formula can be found out as follows :

(i) *Hofmann's methods :* In this method ammonia is oxidised to nitrogen and hydrogen chloride by treatment with chlorine. The experiment is conducted as follows. A long graduated glass tube about 3 ft. long (Fig. 23·6) ; fitted with a stop-cock at one end and dropping funnel at the other, is filled with dry chlorine gas. The tube is marked off into three equal parts by rubber rings. Concentrated solution of ammonia is taken in the funnel and slowly added to chlorine gas drop by drop. An each drop of solution enters the tube a spontaneous vigorous reaction occurs generating flashes of light and producing white fumes of NH_4Cl inside. Sufficient ammonia is added till all the chlorine are used up : $2NH_3+3Cl_2=6HCl+N_2$; $6HCl+6NH_3=6NH_4Cl$

The excess of ammonia is then neutralised by adding dilute sulphuric acid. The tap of the dropping funuel is now closed, and the tube is now placed in a tall jar containing water. The bottom tap is now opened, when water rushes up and fill the tube upto two-thirds of its volume. The remaining one-third is found to contain nitrogen only. It means that the volume of nitrogen produced is one-third of the volume of chlorine used for the experiment.

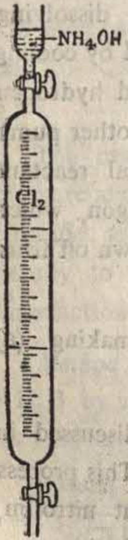


Fig. 23·6
Hofmann's
Experiment

It is known that hydrogen and chlorine combine in equal volumes to form hydrogen chloride : $H_2+Cl_2=2HCl$. So the three volumes of chlorine, consumed in the above experiment, must have combined with three volumes of hydrogen. This hydrogen was provided by the same amount of ammonia which produced simultaneously one volume of nitrogen, filling only one division of the tube. Hence, ammonia is made up of 1 volume of nitrogen and 3 volumes of hydrogen.

The formula of ammonia :

Let 1 volume of nitrogen contains n moleculs, then in ammonia, n molecules of nitrogen combine with $3n$ moleculs of hydrogen (by Avogadro's hypothesis)

or, 1 molecule of nitrogen combines with 3 molecules of hydrogen

or, 2 atom of nitrogen combine with 6 atoms of hydrogen

$$\therefore \frac{\text{Number of atoms of nitrogen in ammonia}}{\text{Number of atoms of hydrogen in ammonia}}=\frac{2}{6}=\frac{1}{3}.$$

Hence the empirical formula of ammonia is NH_3.
Suppose the molecular formula of ammonia is $(NH_3)_x$.

The vapour density of ammonia is found by experiment to be 8·5 and hence the molecular wight is 17.

$\therefore\ (NH_3)_x=17$ or $(14+3)x=17,\ \therefore\ x=1.$
Therefore the molecular formula of ammonia is NH_3.

(ii) *Eudiometric method :* In this method ammonia is first decomposed almost completely to nitrogen and hydrogen by prolonged sparking, the resulting mixture is then exploded with oxygen to yield pure nitrogen and steam. The experiment is conducted as follows.

A measured volume of pure and dry ammonia is collected in an eudiometer over mercury (Fig. 23·7) and sparked until no further change of volume occurs. The final volume after the adjustment of the mercury levels is found to be double the original volume of ammonia. An excess of oxygen is then introduced into the eudiometer and the mixture again sparked when hydrogen is oxidised into water. After Cooling the volume of the residual gas $(N_2+\text{excess } O_2)$ is measured, and the excess oxygen is estimated by treatment with alkaline pyrogallol. Let,

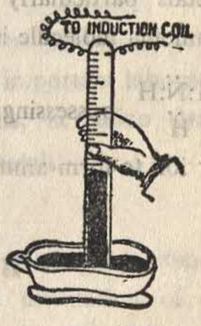


Fig. 27·7.
the Eudiometric method

the volume of ammonia taken for sparking = 20 c.c.

the volume of oxygen taken for further explosion = 20 c.c.

the volume of residual gas after explosion and cooling
(N_2 + excess O_2) = 15 c.c.

the volume of excess oxygen absorbed by pyrogallol = 5 c.c.

Hence the volume of oxygen actually used up = (20 − 5)c.c. = 15cc.

and the volume of nitrogen produced = (15 − 5) c.c. = 10 c.c.

By Avogadro's hypothesis the volume of gases taking part in the above reactions may be written as molecular coefficients in the equation :

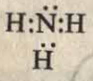
$$20\,N_xH_y + 15O_2 = 10N_2 + \text{water}$$

N_xH_y stands for the molecular formula of ammonia.

Hence 20 atoms of nitrogen have been produced from 20 molecules of ammonia, and therefore $x = 1$. Since the 30 atoms of oxygen used up required 60 atoms of hydrogen to form water, $y = \frac{60}{20} = 3$.

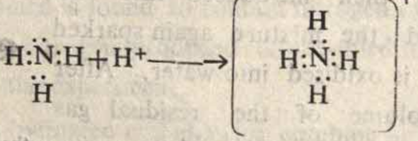
The molecular formula of ammonia is therefore, NH_3. This is confirmed by the experimentally found relative density of the gas 8·5, which show that the molecular weight is 17.

23·8. **Ammonium Salts :** Ammonia (or its aqueous solution NH_4OH) is weak base, and it readily combines with acids to form ammonium salts which are stable compounds, often very similar to and isomorphous with the corresponding salts of alkali metals particularly potassium. The electronic configuration of the ammonia molecule is (See Vol 2)



$$\begin{array}{c} H:\ddot{N}:H \\ \ddot{H} \end{array}$$

possessing a lone pair of electrons, which attracts easily a H^+ ion to form ammonium ion $(NH_4)^+$.



$$\begin{array}{c} H:\ddot{N}:H \\ \ddot{H} \end{array} + H^+ \longrightarrow \left[\begin{array}{c} H \\ H:\ddot{N}:H \\ \ddot{H} \end{array} \right]^+$$

Therefore, $NH_3 + H^+ + Cl^- = NH_4{}^+ + Cl^-$

$$2NH_3 + 2H^+ + SO_4{}^{--} = 2NH_4{}^+ + SO_4{}^{--}$$

This is how ammonia produces different salts. The ammonium salts are very soluble in water and are highly ionised giving monovalent NH_4^+ ion, which behaves like alkali-metal ions (K^+). Alkali liberates ammonia from ammonium salts. Though a few of them decompose on heating, but many sublime when heated. Some ammonium salts are mentioned below.

(i) Ammonium Chloride, NH_4Cl, or Sal Ammoniac.

It is prepared by heating a mixtture of sodium chloride and ammonium sulphate ; the ammonium chloride sublimes :

$$2NaCl + (NH_4)_2SO_4 = Na_2SO_4 + 2NH_4Cl.$$

It is also prepared on a large scale by neutralising ammoniacal liquor from coal gas plant with hydrochloric acid and evaporating the solution to dryness.

Ammonium chloride is a white crystalline solid with a saline taste. It is freely soluble in water with a considerable lowering of temperature as the solution takes place with the absorption of heat. When heated it undergoes thermal dissociation into ammonia and hydrogen chloride :

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

These gases recombine on cooling, and therefore NH_4Cl appears to sublime when heated. When heated with alkalis, ammonium chloride evolves ammonia :

$$NH_5Cl + NaOH = NH_3 + H_2O + NaCl.$$

Ammonium chloride is widely used as an important laboratory reagent, it is used in medicine, in some dry cells, in calico dyeing and printing and also used during soldering of metals.

(ii) Ammonium Sulphate $(NH_4)_2SO_4$.

Ammonium sulphate is prepared by directly passing the ammonia gas produced by Haber's process or destructive distillation of coal into 60 per cent sulphuric acid.

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

But in India, the Fertiliser industry at Sindri (Bihar), produces ammonium sulphate on a large scale by passing ammonia into an aqueous suspension of finely ground gypsum, $CaSO_4$, and bubbling carbondioxide through the suspension.

$$CaSO_4 + 2NH_3 + CO_2 + H_2O = CaCO_3 + (NH_4)_2SO_4.$$

The calcium carbonate is filtered off and the solution is evaporated to obtain crystals of ammonium sulphate.

It forms transparent crystals isomorphous with potassium sulphate and is very soluble in water. It loses ammonia on heating forming ammonium bisulphate :

$$(NH_4)_2SO_4 = NH_4HSO_4 + NH_3.$$

Ammonium sulphate is largely used as a fertiliser in agriculture. It is also used as a laboratory reagent and to produce other ammonium salts.

(iii) Ammonium nitrate, NH_4NO_3.

It is prepared by neutralising ammonium hydroxide with 60% nitric acid and then crystallising the salt from the solution :

$$NH_4OH + HNO_3 = NH_4NO_3 + H_2O.$$

It is also obtained by the double decomposition of ammonium sulphate with calcium nitrate or sodium nitrate in aqueous solution :

$$(NH_4)_2SO_4 + Ca(NO_3)_2 = CaSO_4 + 2NH_4NO_3 ;$$
$$(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2NH_4NO_3.$$

In the frist case, the precipitated calcium sulphate is filtered off, and the ammonium nitrate is crystallised. In the second case, On concentrating and cooling the solution, sodium sulphate separates out first as glauber salt Na_2SO_4, $10H_2O$. Ammonium nitrate crystals are then recovered from the mother liquor.

Ammonium nitrate is a colouless, deliquescent crystalline solid, freely soluble in water. On heating, the salt melts and at 220°C it decomposes into nitrons oxide and water : $NH_4NO_3 = N_2O + 2H_2O$. When stored in bulk, it has a tendency to explode.

Ammonium nitrate is an important nitrogen fertiliser. It is also used in making some explosives ; such as, ammonal (mixture of ammonium nitrate with aluminium powder) and ammatol (mixture of ammonium nitrate with T. N. T.).

(iv) Ammonium carbonate, $(NH_4)_2CO_3$ **or sal-volatile**.

When an intimate mixture of ammonium sulphate and dry chalk powder ($CaCO_3$) is heated, ammonium carbonate sublimes as a white mass.

$$(NH_4)_2SO_4 + CaCO_3 = CaSO_4 + (NH_4)_2CO_3.$$

The sublimate so obtained is largely a mixture of ammonium bicarbonate, NH_4HCO_3, and ammonium carbamate, NH_2COONH_4, but in solution the carbamate is hydrolysed to the normal carbonate, $(NH_4)_2CO_3$.

Ammonium carbonate undergoes slow dissociation even at ordinary temperature :

$$(NH_4)_2CO_3 = 2NH_3 + CO_2 + H_2O.$$

It is used as a reagent in the laboratory and is also a component of *smelling salts.*

(v) **Urea,** $NH_2{\cdot}CO{\cdot}NH_2$,

Urea is the most important nitrogenous fertiliser used. It is prepared by feeding compressed carbondioxide and liquid ammonia (mole ratio 1 : 3) under a pressure of 150—200 atmospheres into an autoclave kept at a temperature of 160° – 180°C, The ammonium carbamate first formed in the liquid reaction mass changes into urea and steam at higher temperature,

$$CO_2 + NH_3 \rightleftharpoons H_2N-CO-ONH_4 \text{ (ammonium carbamate)}$$

$$H_2N-CO-ONH_4 \rightleftharpoons H_2O + H_2N-CO-NH_2 \text{ (urea)}$$

The dry urea is packed and sent to the market as fertiliser,

Exercise—23

1. Describe the method for the preparation of a sample of pure and dry ammonia. What drying agent would you use and why ? Mention some reactions to illustrate its reducing property and basic character. State some of the uses of ammonia.

2. How has the molecular formula of ammonia determined ? Why is Ammonia given the formula NH_3 and not N_2H_6 ? What reasons are there for supposing that ammonia gas combines chemically with water ?

3. Discuss, stating the conditions, the reactions of ammonia with the following :

a) chlorine, b) cupric oxide, c) sodium, d) mercuric chloride, e) silver chloride, f) copper sulphate, g) ferric chloride and h) carbondioxide.

4. How will you prepare nitrogen from ammonia and vice versa ? How may ammonia be converted into nitric acid ? How is ammonia detected ?

5. Give an outline of the process of synthesising ammonia by Haber's method with special reference to the physico chemical principles involved.

6. a) How are the ammonium salts obtained ? How are they detected ? Give your reasons for calling ammonium (NH_4) compound radical.

b) Describe the action of heat upon the following substances,

i) ammonium chloride, ii) ammonium nitrite, iii) ammonium nitrate, iv) ammonium carbonate.

7. a) What nitrogen fertilisers are commonly used ? How are they produced ?

b) How ammonium sulphate is manufactured in our country ?

c) Why ammonia is found suitable as a refrigerant ?

CHAPTER XXIV

OXIDES AND OXYACIDS OF NITROGEN

24 1. Oxides of Nitrogen :—Nitrogen froms a number of oxides. The chief oxides of nitrogen are as follows :

Oxides	Formula	Mol. wt.	Oxidation no. of nitrogen
Nitrous oxide	N_2O	44	+1
Nitric oxide	NO	30	+2
Nitrogen trioxide	N_2O_3	76	+3
Nitrogen tetroxide	N_2O_4	92	+4
(Nitrogen dioxide)	(NO_2)	(46)	(+4)
Nitrogen pentoxide	N_2O_5	108	+5

24 2. Nitrous Oxide, N_2O : The gas was discovered by priestley but is was carefully studied by Davy. On account of the hysterical symptoms resulting from its inhalation, the gas is commonly called *laughing gas.*

Preparation : Nitrous oxide is usually prepared in the laboratory by cautiously heating dry ammonium nitrate (or a mixture of ammonium sulphate and sodium nitrate) in a round-bottomed flask fitted with a cork and a delivery tube (Fig 24·1). The temperature should not exceed 200°C as overheating may lead to explosion. The nitrate decomposes, yielding nitrous oxide and water :

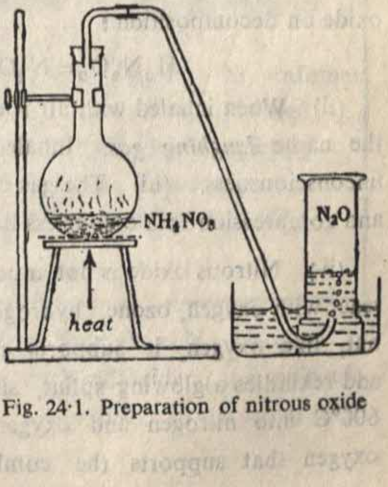


Fig. 24·1. Preparation of nitrous oxide

$$(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2NH_4NO_3$$

$$NH_4NO_3 = N_2O + 2H_2O.$$

As the gas is appreciably soluble in cold water, it is collected over hot water, or over mercury.

The gas thus produced is not pure. It contains nitrogen, higher oxides of nitrogen, chlorine (due to the prescence of a little NH_4Cl in the nitrate) and moisture. To obtain pure N_2O it is washed by passing through (i) caustic soda solution to remove NO_2,Cl_2 etc., (ii) ferrous sulphate solution to remove NO and (iii) concentrated sulphuric acid to remove moisture and ammonia, and then collected over mercury. It may still contain some nitrogen.

Very pure nitrous oxide may be prepared by mixing solutions of hydroxylamine hydrochloride and sodium nitrite :

$$NH_2OH, HCl+NaNO_2=N_2O+NaCl+2H_2O.$$

N.B. In NH_4NO_3, nitrogen has two oxidation states, namely -3 and $+5$, which disproportionates to N_2O in which nitrogen has the oxidation state of $+1$.

Properties :—(i) nitrous oxide is a colourless neutral gas, having a faint and pleasant odour and a sweetish taste. It is 1·5 times heavier than air and considerable soluble in cold water and more in alcohol, but insoluble in hot water. Its aqueous solution is neutral to litmus hence it is a neutral oxide and does not behave as the anhydride of hyponitrous acid, which, however, yields nitrous oxide on decomposition :

$$H_2N_2O_2=N_2O+H_2O$$

(ii) When inhaled with air it causes hysteric laughter and hence the name *laughing gas*. Inhaled in pure state or in excess it causes unconsciousness. (iii) The gas can be liquefied easily by cooling and compression to a colourless liquid, b.p. $-88.7°C$.

(iv) Nitrous oxide is not much chemically active. It does not react with oxygen, ozone, hydrogen, chlorine etc. It does not burn but, like oxygen, it supports combustion of burning substances and rekindles a glowing splint, since it readily decomposes above 600°C into nitrogen and oxygen : $2N_2O=2N_2+O_2$. It is this oxygen that supports the combustion. In decomposed nitrous oxide, $N_2 : O_2$ ratio is 2 : 1. The percentage of oxygen here is thus higher than in air. So nitrous oxide support combustion more vigorously than air. Thus burning pieces of charcoal, phosphorus, sulphur and heated metals such as sodium, potassium, magnessium etc, burn brilliantly in the gas—the heat decomposing the gas with the liberation of oxygen which supports combustion.

$$2N_2O + C = CO_2 + 2N_2 \; ; \; 2P + 5N_2O = P_2O_5 + 5N_2$$
$$2N_2O + S = SO_2 + 2N_2 \; ; \; N_2O + 2Na = Na_2O + N_2.$$

(v) When nitrous oxide is passed over heated iron or copper, the latter are oxidised and nitrogen is set free.

$$Cu + N_2O = CuO + N_2 \; ; \; 2Fe + 3N_2O = Fe_2O_3 + 3N_2.$$

Uses : Nitrous oxide is often used for anaesthesia in surgery. It is also used in preparing whipped cream.

Oxygen and nitrous oxide are both colourless gases and both of them support combustion vigorously and rekindle a glowing splint. The following properties, however, serve to distinguish nitrous oxide from oxygen :

Properties	Nitrous oxide	Oxygen
1. Density (H = 1)	22	16
2. Solubility in cold water.	Fairly soluble	Searcely soluble
3. Solubility in alkal.ne pyrogallate	insoluble	Reanily absorbed
4. Reactlon with nitric oxide	No reaetion	Reddish brow nfumes of NO_2 formed
5. Volume change when phosphorus burns in gas	No change ; as an equal volume of nitrogen is liberated, $2P + 5N_2O = P_2O_5 + 5N_2$	Gas completely absorbed, $4P + 5O_2 = 2P_2O_5$

N_2O molucule is linear, is structural formula is $\overset{-}{N} = \overset{+}{N} = O$.

Nitrous oxide closely resembles carbondioxide (the molecule $O = C = O$ is also linear) in physical properties. In the solid state these are isomorphous.

24.3. Nitric Oxide NO. This gas was first prepared by Helmont in the early part of the seventeenth century, but Priestley was the first to study it.

Preparation : Nitric oxide is formed in small quantities when a mixture of oxygen and nitrogen is subjected to a spark discharge : $N_2+O_2 \rightleftharpoons 2NO-43·2KCal$. It is prepared in the laboratory by the action of moderately concentrated (1 : 1) nitric acid on copper turnings at ordinary temperature :

$$3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO\uparrow.$$

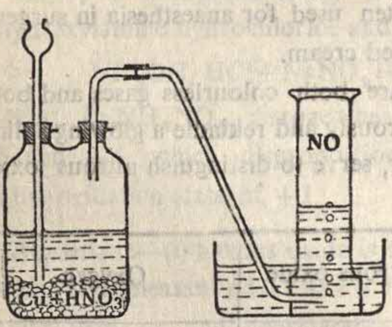


Fig. 24·2. Preparation of nitric oxide

Some copper turning are taken in a woulfe's bottle fitted with a thistle funnel and a delivery tube, the outer end of the delivery tube dips under water in a pneumatic trough, (Fig 24.2). Moderately concentrated nitric acid (1 : 1) is then poured through the thistle funnel, so that the end of the funnel dips below the surface of the liquid. Action immediately sets in and nitric oxide is evolved at the ordinary temperature, which produces reddish-brown fumes of NO_2 gas with the air in the bottle. The brown fumes are first allowed to escape and the colourless nitric oxide gas is collected in gas jars by displacement of water. The gas thus prepared is not pure and is liable to be contaminated with other oxides of nitrogen. To purify, it is passed through ferrous sulphate solution which absorbs nitric oxide alone forming dark brown solution of $Fe(NO)SO_4$ – a nitroso compound, which on gentle heating evolves nearly pure nitric oxide.

Pure nitric oxide is also obtained by warming a mixture of potassium nitrate and sulphuric acid with either ferrous sulphate or mercury.

(a) $2KNO_3+4H_2SO_4+6FeSO_4=3Fe_2(SO_4)_3+K_2SO_4+4H_2O+2NO$

(b) $2KNO_3+4H_2SO_4+6Hg=3Hg_2SO_4+K_2SO_4+4H_2O+2NO$

Properties : (i) Nitric oxide is a colourless gas, slightly heavier than air and sparingly soluble in water. It is a neutral oxide like nitrous oxide.

(ii) It is not combustible. The gas itself is quite stable and decomposes only at 1000°C into nitrogen and oxygen : $2NO = N_2 + O_2$.

Consequently, nitric oxide ordinarily does not support combustion. Feebly burning phosphorus, burning sulphur or charcoal or a lighted taper are, therefore, extinguished in the gas. But vigorously burning phosphorus, charcoal, magnesium or boiling sulphur continues to burn in the gas—the heat being sufficient to decompose nitric oxide and the oxygen produced supports combustion.

$$4P + 10NO = 2P_2O_5 + 5N_2.$$

(iii) Nitric oxide combines spontaneously with oxygen to give reddish brown fumes of nitrogen dioxide,

$$2NO + O_2 = 2NO_2$$

It also combines with chlorine in the presence of charcoal to form nitrosyl chloride and with bromine to give nitrosyl bromide : $2NO + Cl_2 = 2NOCl$; $2NO + Br_2 = 2NOBr$.

(iv) Nitric oxide is readily soluble in cold ferrous sulphate solution to yield a dark brown solution cantaining the unstable complex compound ferrous nitroso sulphate $Fe(NO)SO_4$. On heating the solution, the complex breaks up and NO is librated,

$$FeSO_4 + NO = [Fe(NO)]SO_4 \; ; \; [Fe(NO)]SO_4 = FeSO_4 + NO.$$

(v) Nitric oxide is an *oxidising agent*. It can be reduced in a variety of ways depending on the nature of the reducing agent employed. Red-hot iron, copper, nickel or carbon give free nitrogen ; hydrogen in the presence of heated platinum gives ammonia ; tin and hydrochloric acid give hydroxylamine ; sulphurous acid or sulphuretted hydrogen gives nitrous oxide.

$2Cu + 2NO = 2CuO + N_2$; $2Ni + 2NO = 2NiO + N_2$

$5H_2 + 2NO = 2NH_3 + 2H_2O$; $NO + 3H(Sn + HCl) = NH_2OH$

$2NO + H_2SO_3 = N_2O + H_2SO_4$; $2NO + H_2S = H_2O + S + N_2O$.

(vi) But to a powerful oxidising agent, it acts as a *reducing agent.* Thus oxidising agents like potassium permanganate, potassium dichromate and even iodine oxidise nitric oxide to nitric acid.

$$6KMnO_4+9H_2SO_4+10NO=3K_2SO_4+6MnSO_4+10HNO_3+4H_2O$$

$$3I_2+2NO+4H_2O=2HNO_3+6HI.$$

N.B. Nitric oxide, NO, contains nitrogen in an intermediate oxidation state. So it acts as both oxidant and reductant.

Uses :—It is used as an oxygen carrier in the preparation of H_2SO_4 by the chamber process.

Test :—(i) With oxygen nitric oxide immediately turns reddish-drown ; (ii) nitric oxide turns ferrous sulphate solution dark brown ; (iii) A mixture of nitric oxide and carbon disulphide vapour burns with a brilliant bluish flame when ignited :

$$2CS_2+10NO=2CO+4SO_2+5N_2.$$

The NO molecule contains an odd electron in its strueture $:\dot{N}::\ddot{O}:$ or $\dot{N}=O$

24.4. Composition of Nitrous oxide and Nitric oxide :

The volumetric composition of both the oxides can be determined in the similar way by heating a spiral of iron wire in a measured volume of the gas. The experiment is done as follows : A volume of the gaseous oxide is collected over mercury in a tube, the upper end of which is closed by a cork through which pass a pair of platinum wires connected together by a spiral of iron wire inside the tube. The volume of the gas is noted (Fig 24.3). The iron wire is then heated elcctrically by connecting the two pt-wries to the terminals of a battery. The hot iron decomposes the gaseous oxide forming solid Fe_2O_3 and liberating nitrogen gas whose volume is noted after adjusting the mercury levels. By actual experimentit is found that,

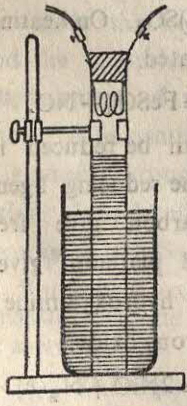


Fig. 24·3. Iron wire experiment

the volume remains unchanged if nitrous oxide is taken in the tube. But when nitric oxide is taken, the nitrogen produced has a volume which is half of that of the oxide taken.

Formula of Nitrous oxide : It is found that nitrous oxide contains its own volume of nitrogen, Hence,

1 volume nitrous oxide contains 1 volume nitrogen,

$\therefore$ by Avogadro's hypothesis,

n molecules of nitrous oxide contain n molecules of nitrogen,

or, 1 molecule of nitrous oxide contains 1 molecule or 2 atoms of nitrogen.

Hence the formula is N_2O_x and the mol. wt. $= 28+16x$.

But the vapour density of nitrous oxide is 22.

i.e the molecular weight $= 2 \times 22 = 44$.

$\therefore \ 28+16x=44, \quad \text{or} \quad x=1.$

Hence the molecular formula of nitrous oxide is N_2O.

Formula of Nitric oxide : It is found that nitric oxide contains half its own volume of nitrogen, Hence,

1 volume of nitric oxide contains $\frac{1}{2}$ volume of nitrogen.

$\therefore$ by Avogadro's hypothesis,

1 molecule of nitric oxide contains $\frac{1}{2}$ molecule or 1 atom of nitrogen.

So the formula is NO_x and the mol. wt. $= 14+16x$.

But the vapour density of nitric oxide $= 15$,

i.e the molecular weight $= 2 \times 15 = 30$.

$\therefore \ 14+16x=30, \quad \text{or} \quad x=1.$

Hence the molecular formula of nitric oxide is NO.

24 5. Nitrogen Trioxide, N_2O_3 or Nitrous Anhydride :

Preparation :—It may be prepared by distilling together equal weights of arsenious oxide and nitric acid (60%), and condensing the vapours into a dark blue liquid in a receiver cooled in freezing mixture :

$$As_2O_3+2HNO_3+2H_2O=2H_3AsO_4+N_2O_3\uparrow.$$

A portion of nitrogen trioxide remains dissociated as

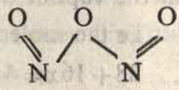
$$2N_2O_3 \rightleftharpoons 2NO+N_2O_4.$$

Nitrogen trioxide is also formed when an equimolar mixture of NO_2 and NO is cooled to a very low temperature (–30°C).

Properties :—Nitrogen trioxide is an unstable compound. It may be obtained at a very low temperature in the form of blue crystals. At –102° these crystals melt, and at once begin to dissociate, $2N_2O_3 \rightleftharpoons 2NO + N_2O_4$. At room temperature the reddish-brown gas contains only 10 per cent. of undissociated molecules of N_2O_3 ; at 100° dissociation is complete. It forms nitrous acid with ice cold water and reacts with caustic alkalis forming nitrites. It is thus the anhydride of nitrous acid.

$$N_2O_3 + H_2O = 2HNO_2 \; ; \; N_2O_3 + 2NaOH = 2NaNO_2 + H_2O$$

The structural formula of nitrogen trioxide is



24·6. Nitrogen Dioxide, NO_2 and Nitrogen Tetroxide, N_2O_4 :

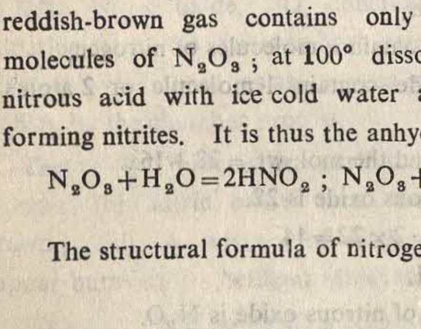


Fig. 24·4. Preparation of nitrogen tetroxide ;

preparation :—In the laboratory nitrogen dioxide is conveniently prepared by heating dry powdered lead nitrate in a hard glass test tube. When carefully heated, lead nitrate decomposes into reddish brown nitrogen dioxide (NO_2) gas and oxygen. The gaseous product is then led through a U-tube kept cooled by a freezing mixture. (Fig 24.4). on cooling, nitrogen dioxide condenses into a pale yellow liquid in the U-tube and oxygen passes out. This yellow liquid consists mostly of nitrogen tetroxide (N_2O_4) molecules.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$
$$2NO_2 \rightleftharpoons N_2O_4.$$

Nitrogen dioxide is readily formed by the reaction of nitric oxide (2 vols) and oxygen (1 vol) : $2NO + O_2 = 2NO_2$.

Properties :—(i) Pure nitrogen tetroxide (N_2O_4) occurs as colourless crystals below $-10°C$. With the rise of temperature, when the crystals melt, it begins to decompose into nitrogen dioxide (NO_2) molecules, and the pale yellow liquid may be considered as a dilute solution of NO_2 in N_2O_4. The liquid boils at 22°C. At about 25°C, the gas is brownish red containing nearly 20% NO_2 and 80% N_2O_4 molecules. The colour of NO_2 molecules is reddish brown. The dissociation is practically complete at about 150°C and the gas consists entirly of NO_2 molecules: $N_2O_4 \rightleftharpoons 2NO_2$. During heating the colour deepens gradually from yellow to reddish-brown—the colour change accompanies a decrease in density up to 150°C, when the density becomes constant and corresponds with NO_2. Above 150°C again the colour becomes paler due to further dissociation of nitrogen dioxide into nitric oxide and oxygen; $2NO_2 \rightleftharpoons 2NO+O_2$ and also the density decreases, until at about 620°C, the gas is colourless when the dissociation becomes complete. The reverse charge takes place on cooling.

$$\underset{\text{(solid)}}{N_2O_4} \overset{-10^\circ C}{\rightleftharpoons} \underset{\text{(liq.)}}{N_2O_4} \overset{22^\circ C}{\rightleftharpoons} \underset{\text{(vapour)}}{N_2O_4} \overset{150^\circ C}{\rightleftharpoons} \underset{\text{(gas)}}{2NO_2} \overset{620^\circ C}{\rightleftharpoons} 2NO+O_2$$

(ii) It is not combustible nor supports burning readily. But vigorously burning phosphorus, sulphur and charcoal continue to burn in the gas yielding their oxides and free nitrogen. Potassium spontaneously inflames when brought in contact with nitrogen dioxide.

$$K+2NO_2=KNO_3+NO.$$

(iii) Nitrogen dioxide is regarded as a mixed anhydride of nitrous and nitric acid, as both the acids are formed when nitrogen dioxide dissolves in water :

$$2NO_2+H_2O=HNO_3+HNO_2.$$

But the nitrous acid decomposes, giving nitric acid and nitric oxide :

$$3HNO_2=HNO_3+H_2O+2NO.$$

Hence the ultimate products are nitric acid and nitric oxide :

$$3NO_2+H_2O=2HNO_3+NO.$$

Nitrogen dioxide is absorbed by alkalis to produce equivalent quantities of nitrate and nitrite :

$$2KOH+2NO_2=KNO_3+KNO_2+H_2O.$$

(iv) Nitrogen dioxide behaves as a good oxidising agent, which takes part in many reactions by giving up either the whole or part of its oxygen to a reducing agent, bearing a residue of nitrogen or nitric oxide. Thus it easily oxidises KI, H_2S, SO_2, CO, etc., itself being reduced to nitric oxide.

$$2KI+NO_2+H_2O=I_2+2KOH+NO$$
$$H_2S+NO_2=S+H_2O+NO$$
$$SO_2+NO_2+H_2O=H_2SO_4+NO$$
$$CO+NO_2=CO_2+NO.$$

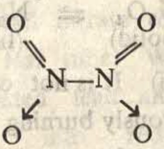
It may be reduced to nitrogen when passed over heated metals like iron or copper :

$$2NO_2+4Cu=4CuO+N_2$$

(v) The gas is absorbed by concentrated sulphuric acid forming nitroso sulphuric acid.

$$2NO_2+H_2SO_4=SO_2(HO)ONO+HNO_3$$

The structure of nitrogen tetroxide is given as



24·7. Nitrogen Pentoxide, N_2O_5.

Preparation :—Nitrogen pentoxide, being the anhydride of nitric acid, may be prepared by careful dehydration of nitric acid with phosphorus pentoxide : $2HNO_3+P_2O_5=2HPO_3+N_2O_5$. Phosphorus pentoxide is added, in small quantities at a time, to a little less than its own weight of purified nitric acid cooled in a freezing mixture. The pasty mass is then transferred to a retort and gently distilled. The distillate of nitrogen pentoxide is collected in ice-cold bottles where it condenses as colourless crystals.

Nitrogen pentoxide may also be prepared (i) by the action of chlorine on solid silver nitrate :

$$4AgNO_3+2Cl_2=4AgCl+2N_2O_5+O_2$$

(ii) By passing ozonised oxygen through cooled liquid nitrogen tetroxide :

$$N_2O_4+O_3=N_2O_5+O_2$$

Properties :—(i) Nitrogen pentoxide crystallises in brilliant colourless transparent crystals, which melt with some decomposition at about 30°C. Nitrogen pentoxide is stable below 0°C, but at higher temperatures decomposition occurs, becoming rapid at 50°C :

$$2N_2O_5 \rightleftharpoons 2N_2O_4+O_2$$

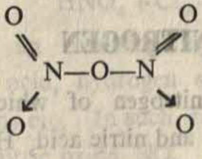
(ii) It is an anhydride of nitric acid, it dissolves in water forming nitric acid :

$$N_2O_5+H_2O=2HNO_3.$$

(iii) Phosphorus, sodium and potassium burn in liquid nitrogen pentoxide if warmed ; charcoal is not attacked by the liquid, but it burns brilliantly in the vapour.

(iv) It is a powerful oxidising agent. Iodine is oxidised to iodine pentoxide by N_2O_5. It attacks many organic substances with violence.

The structural formula of nitrogen pentoxide in the vapour state is



24·8. Comparison of Oxides of nitrogen :

(i) *Physical properties* :—All the oxides of nitrogen are gaseous at the ordinary temperature except N_2O_5 which is a colourless solid. Of the gaseous oxides, N_2O and NO is colourless and N_2O_3 and NO_2 are reddish brown.

(ii) *Solubility in water and action with litmus* :—N_2O, a neutral oxide, is soluble in cold water, NO is also neutral oxide and slightly soluble. The other oxides dissolve in water, yielding acids, hence they are acidic oxides.

(iii) *Action of alkalis* :—N_2O and NO do not react with alkalis as they are neutral oxides. The other three oxides, however react with alkalis—N_2O_3 producing nitrites, N_2O_4 producing both nitrites and nitrates and N_2O_5 yields nitrates.

(*iv*) *Combustibility*, *Oxidising properties* :—All the oxides are non-combustible. N_2O, like oxygen ; readily supports combustion, while the other oxides do not normally support combustion. But vigorously burning phosphorus, sulphur, charcoal etc., continue to burn in these gases, as the heat produced during burning is sufficient to decompose the oxides liberating oxygen which supports combustion. The oxides also act as oxidising agents, while NO, containing nitrogen in an intermediate oxidation state, acts both as oxidising and reducing agent.

(*v*) *Absorbents* :—N_2O is absorbed by alcohol, NO by cold ferrous sulphate solution. The other three oxides, being acidic, are absorbed by alkalis.

(*vi*) *Physiological activity* :—All the oxides are poisonous. N_2O, when inhaled with air, causes hysteric laughter and is a mild anaesthetic.

OXY-ACIDS OF NITROGEN

There are several oxy-acids of nitrogen of which two are important, namely nitrous acid, HNO_2 and nitric acid, HNO_3.

24·9. Nitrous Acid, HNO_2 : Free nitrous acid is very unstable and so cannot be obtained in the pure state. Only its salts or its aqueous solution can be prepared.

Preparation : It may be prepared in solution by the action of cold dilute sulphuric acid on barium nitrite solution. $BaSO_4$ is precipitated, filtered and an aqueous solution of nitrous acid is obtained.

$$Ba(NO_2)_2 + H_2SO_4 = BaSO_4 + 2HNO_2.$$

On standing, nitrous acid in solution is slowly changed into nitric acid and nitric oxide : $3HNO_2 = HNO_3 + 2NO + H_2O$.

This is an example of *disproportionation.* In HNO_2, the oxidation state of nitrogen is +3. During the change, it is converted into NO (oxidation state of N is +2) and HNO_3 (oxidation state of N is +5), i.e. a mixture of lower and higher oxidation state.

Nitrous acid is also formed in solution when ice-cold solutions of sodium (or potassium) nitrite and hydrochloric acid are mixed :

$$NaNO_2+HCl=NaCl+HNO_2$$

Properties :—(i) The freshly prepared solution of nitrous acid, has a pale blue colour. It is weak monobasic acid, which slowly decomposes, giving brown fumes of oxides of nitrogen : $2HNO_2 \rightleftharpoons H_2O+N_2O_3$; $N_2O_3 \rightleftharpoons NO+NO_2$. Small amount of nitric acid is also formed during the decomposition due to disproportionation : $3HNO_2=HNO_3+2NO+H_2O$. (ii) Nitrous acid acts both as a reducing agent as well as an oxidising agent.

(a) As a reducing agent, it reduces acidified permanganate solution, hydrogen peroxide, chlorine or bromine water etc. In such reactions, nitrous acid always oxidised to nitric acid.

$$5HNO_2+2KMnO_4+3H_2SO_4=5HNO_3+K_2SO_4+2MnSO_4+3H_2O$$

$$HNO_2+H_2O_2=HNO_3+H_2O.$$

$$HNO_2+Cl_2+H_2O=HNO_3+2HCl$$

(b) As an oxidising agent, it oxidises potassium iodide, sulphurous acid, hydrogen sulphide, ferrous and stannous salts in acid solutions etc, In such reactions nitrous acid itself is always reduced to nitric oxide, NO.

$$2HNO_2+2KI+2H_2SO_4=2K_2SO_4+I_2+2NO+2H_2O.$$

$$2HNO_2+H_2SO_3=H_2SO_4+2NO+H_2O$$

$$2HNO_2+H_2S=S+2NO+2H_2O$$

$$2HNO_2+2FeSO_4+H_2SO_4=Fe_2(SO_4)_3+2NO+2H_2O$$

$$2HNO_2+SnCl_2+2HCl=SnCl_4+2NO+2H_2O$$

(iii) Nitrous acid is decomposed to nitrogen by ammonium chloride and urea on heating :

$$HNO_2+NH_4Cl=N_2+2H_2O+HCl$$

$$2HNO_2+NH_2CONH_2=2N_2+CO_2+3H_2O$$

This reaction is used to remove nitrous acid from a solution.

Uses :—Nitrous acid (prepared in situ) is used in diazotisation reaction in organic chemistry and in dye industry.

The structure of nitrous acid and the nitrite ion are as follows :

$$H-O-N=O\,; \qquad [\,O-N=O\,]^-.$$

Nitrites :—The salts of nitrous acid, i.e., nitrites are more stable and are easily prepared. Nitrites of alkali metals like sodium and potassium are prepared by heating the corresponding nitrates, either alone or with metallic lead.

$$2KNO_3=2KNO_2+O_2$$

$$NaNO_3+Pb=NaNO_2+PbO.$$

The alkali nitrites decompose at high temperature with liberation of nitric oxide and nitrogen :

$$3NaNO_2=Na_2O+NaNO_3+2NO$$

$$5NaNO_2=Na_2O+3NaNO_3+N_2$$

Sodium nitrite is used in large amounts in dye industry.

Tests for nitrous acid and nitrites :—(a) Solid nitrites when treated with dilute acids give reddish brown fumes of nitrogen dioxide.

(b) Nitrous acid or nitrites in acid solution liberates iodine from potassium iodide solution which turn starch solution blue.

(c) An intense pink colour produced by a mixture of solutions of sulphanilic acid and $\alpha-$ naphthylamine in acetic acid is a sensitive test for nitrites or nitrous acid solution.

(d) An acidified solution of a nitrite gives a brown colour with a solution of meta-phenylene-diamine. The presence of nitrite in drinking water is detected by this test.

24·10. Nitric acid, HNO_3 (Aqua fortis) : This acid, called aqua fortis, was known to alchemists, they used it in the separation of gold from silver. Lavoisier (1776) showed that it was a compound containing oxygen.

Free nitric acid, produced by lightning, occurs in traces in the atmosphere. It is found in the form of nitre (potassium nitrate) in the soil of tropical countries like India and as sodium nitrate (chile salt petre) in chile.

Preparation :—*Laboratory method* : Nitric acid is a volatile acid. It is, therefore, expelled from a nitrate by the action of less volalile acid, like concentrated sulphuric acid. Hydrochloric acid is not used since hydrochloric acid is itself volatile though stronger than sulphuric acid. It is generally prepared in the laboratory by distilling a mixture of potassium (or sodium) nitrate with concentrated sulphuric acid.

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

A mixture of equal parts by weight of potassium (or sodium) nitrate and concentrated sulphuric acid is taken in a glass-stoppered report, the stem of which enters into a water-cooled receiver (Fig 24.5). On heating at about 200°C the vapours of nitric acid distil over to the receiver and is collected there as a pale yellow liquid. The yellow colour of the acid is due to dissolved oxides of nitrogen (NO_2) produced from the partial decomposition of the nitric acid. Some water also remain mixed with the acid. It may be concentrated upto 98% by distillation with concentrated sulphuric acid ; oxides of nitrogen may be removed by passing a current of dry air through the acid till colourless. Pure nitric acid is made by freezing the 98% acid at $-42°C$, it is deposited as colourless crystals.

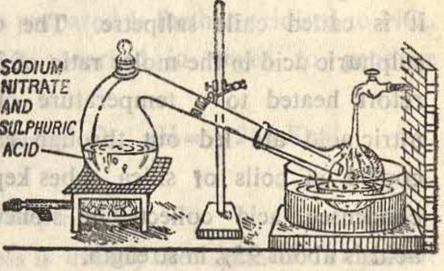


Fig. 24·4. Laboratory preparation of nitric acid

N.B. With excess of potassium nitrate and at a higher temperature, further amount of nitric acid can be produced :

$$KNO_3 + KHSO_4 = K_2SO_4 + HNO_3.$$

But this is generally avoided, for, (i) higher temperature would involve decomposition of the acid, (ii) there is a chance of cracking of the glass retort at such a high temperature and (iii) the removal of mass of the normal sulphate, K_2SO_4 (when solidified) proves quite difficult.

Nitric acid is required for many chemical industries and especially for preparing several kinds of explosives. It is therefore produced in largic quantities.

24.11. Manufacture of Nitric Acid : On the industrial scale nitric acide is produced by the following two proeesses.

(i) Distillation process ; from chile saltpetre.

(ii) Ostwald's process ; from oxidation of ammonia.

At one time, a method of combining oxygen and nitrogen in air into nitric oxide and converting the latter into nitric acid was developed in the Birkeland—Eyde process. But it has now been abandoned for its high cost of production.

1. From Chile Saltpetre : Huge deposits of sodium nitrate, $NaNO_3$ are found along the sea-coasts of Chile in South America ; it is called chile saltpetre. The chile saltpetre and concentrated sulphuric acid in the molar ratio of 3 : 2 are taken in a big cast-iron retort heated to a temperature of 200~250°C. The vapours of nitric acid are led out through earthenware or silica pipes and cooled in coils of silica tubes kept immersed in cold water. The condensed acid collects in stoneware bottles. (Fig 24·6). The acid is about 95% in strength.

$$3NaNO_3 + 2H_2SO_4 = Na_2SO_4 + NaHSO_4 + 3HNO_3.$$

Any uncondensed vapour, which is largely nitrogen dioxide (from the decomposition of nitric acid), passes snto a vertical tower packed with glass balls. Water trickles down the tower and absorbs the vaporus to form dilute nitric acid, which collects in a tank at the bottom of the tower.

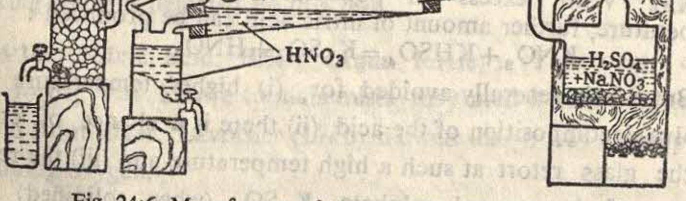


Fig. 24·6. Manufacture of HNO_3 from chile saltpetre

$$4NO_2 + O_2 + 2H_2O = 4HNO_3$$

After the reaction, the mixture of sodium sulphate and bisulphate which remains in the retort is run out in the fluid state. When solid it is known as *nitre-cake.*

In India, a considerable amount of nitric acid is manufactured by this method. It is, of course, dependent on imported chile saltpetre.

2. **From ammonia : Ostwald's process** : Nitric acid is now-a-days extensively manufactured by this process. In this process ammonia is oxidised to nitric oxide by the oxygen of air in presence of heated *platinum gauze catalyst.* The reaction is strongly exothermic. Nitric oxide thus prepared is further oxidised to NO_2 by oxygen of the air which is absorbed in water to produee nitric acid.

$$4NH_3+5O_2=4NO+6H_2O\ ;\ \Delta H=-215\ \text{Kcal.}$$
$$2NO+O_2=2NO_2$$
$$3NO_2+H_2O=2HNO_3+NO.$$

Ammonia gas used in this process is usually the synthetic ammonia obtained from Haber's plant. Atmospheric air is used after preheating it to about 500°C in a heat-exchanger by the hot gases formed by the oxidation of ammonia and then freeing it from dust particles by passing through woolen cloth in an air-filter.

A mixture of pure and dry ammonia and the pre-heated dust free air in the ratio of 1 : 8 by volume, is rapidly passed through a layer of fine-mesh *platinum gauze catalyst* stretched across on an aluminium box, called the converter. (Fig 24·7). The catalyst is initially heated electrically to about 800°C~900°C, but later on, the temperature is maintained by the heat of the reaction. No further external heat is necessary. More than 90% of ammonia is oxidised to nitric oxide. The gases must be swiftly led though the catalyst (time of contact is 0·03 second or less), otherwise ammonia may be oxidised to nitrogen. The reaction occurs under ordinary pressure.

The gases coming out of the converter contains nitric oxide, steam and excess of air. This gas mixture then enters into the heat exchanger and gives away its heat to preheat the in coming air of the reaction and becomes some what cooled. It then enters an empty aluminium or stainless steel cylinder, where it is further cooled to about 50°C. Here, nitric oxide is oxidised to nitrogen dioxide by the oxygen of the accompanying excess air.

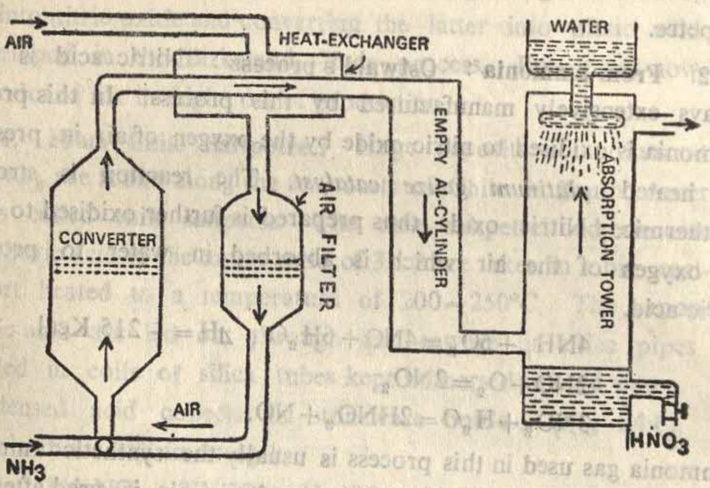


Fig. 24·7. Manufacture of HNO_3 by ostwald's process

The nitrogen dioxide is then absorbed in water in several stainless steel absorption towers packed with broken quartz to form nitric acid. The nitric oxide liberated in this reaction is reoxidised by the air presnt forming NO_2 which re.enters the reaction. Finally the escaping gases are absorbed in a tower with dilute NaOH solution :

$$2NaOH + NO + NO_2 = 2NaNO_2 + H_2O.$$

In the absorption towers a stream of water meets the nitrogen dioxide on the counter-current principle. Water is sprayed from the top of the last tower cf a series of six, and the dilute nitric acid collected from the bottom of this tower is sprayed down the fifth tower, nitric acid from the bottom of the fifth tower is sprayed down the fourth, and so on. The mixture of nitrogen dioxide and air enters at the box of the first tower and passed successively through the series, as shown in Fig 24.8. A 50 per cent. solution of nitric acid is collected from the bottom of the first tower.

The dilute acid may be concentrated by distillation to attain 68 per cent. strength. This is sold in the market as the commercial

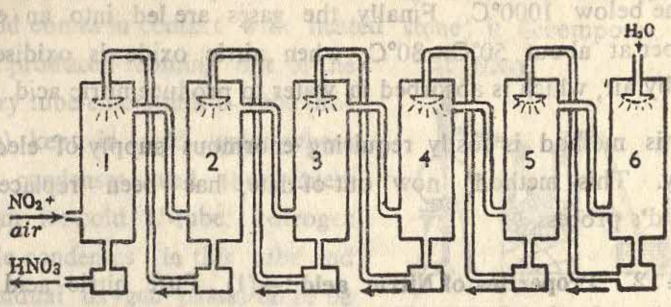


Fig. 24·8. Absorption of NO_2 to produce HNO_3

acid of sp. gr. 1·41. For more concentrated acid, it has to be redistilled with conc. H_2SO_4 at low pressures.

3. From air by Birkeland-Eyde Process :

In this process the atmospheric nitrogen and oxygen are allowed to combine at the high temperature of an electric arc (temp. above 3000°C) to produce about 5% of nitric oxide (Fig 24.9).

$$N_2 + O_2 = 2NO \; ; \; \Delta H = +43{\cdot}2 \text{ Kcal.}$$

Since it is an endothermic reaction, very high temperature is required, hence the use of electric arc. The nitric oxide produced has to be rapidly cooled down other wise with slow fall of temperature it would decompose back to nitrogen and oxygen. For this

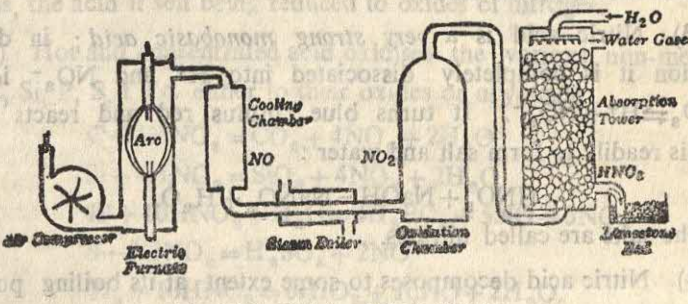


Fig. 24·9. Birkeland-Eyde Process

reason, the gases are swept away immediately after passing the arc and the gas mixture is quickly chilled to less than 1000°C when the rate of decomposition of NO is very slow. Infact, the percentage of nitric oxide which is available in the stable state is about 1% by volume below 1000°C. Finally the gases are led into an empty chamber at about 50°C ~ 80°C, when nitric oxide is oxidised to NO_2 by air, which is absorbed in water to produce nitric acid.

This method is costly requiring enormous supply of electrical energy. This method, now out-of-date, has been replaced by ostwald's process.

24·12. Properties of Nitric acid :—(1) Pure nitric acid is a colourless fuming liquid (sp. gr. 1·52) with a choking smell, boiling at 86°C and freezing at $-41°C$ into a transparent crystalline mass. Nitric acid is miscible with water in all proportions.

(2) When concentrated nitric acid is distilled it undergoes partial decomposition : $4HNO_3 = 2H_2O + 4NO_2 + O_2$. The proportion of water in the acid increases and finally an acid of 68% strength (sp. gr. 1·41) distils over at 121°C. This is the commercial nitric acid. Such a commercial acid is generally prepared by concentrating the dilute nitric acid obtained from its industrial preparation by distillation.

The concentrated (98%) nitric acid coloured reddish brown due to excess of nitrogen dioxide dissolved in it, is known as *fuming nitric acid*. It is a corrosive liquid and causes blisters on the skin with a yellow stain.

(3) Nitric acid is a *very strong monobasic acid* ; in dilute solution it is completely dissociated into H^+ and NO_3^- ions : $HNO_3 \rightleftharpoons H^+ + NO_3^-$. It turns blue litmus red and reacts with alkalis readily to form salt and water :

$$HNO_3 + NaOH = NaNO_3 + H_2O.$$

The salts are called nitrates.

(4) Nitric acid decomposes to some extent at its boiling point ; at higher temperatures the decomposition is very rapid and marked. It decomposes into oxygen, nitrogen dioxide and water :

$$4HNO_3 = 4NO_2 + O_2 + 2H_2O.$$

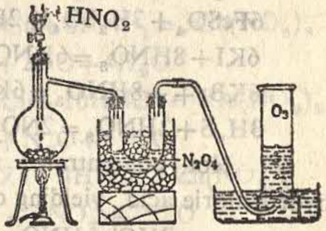


Fig 24·10. Decomposition of nitric acid

Experiment : Conc. HNO_3 is allowed to fall drop by drop on red hot pumice stone kept in a distilling flask. As each drop of the acid comes in contact with heated stone, it decomposes. The gases produced coming out of the delivery tube enters in a u- tube (not shown) kept in cold water where steam condenses and then enters into an ice-cold U-tube. Nitrogen dioxide condenses in this tube and the residual oxygen passes on to be collected over water in a gass jar (Fig 24.10). The condensed nitrogen dioxide may be vaporised separately and passed over heated copper, when nitrogen would be produced : $2NO_2+4Cu=4CuO+N_2$. The oxygen and nitrogen gases thus produced may be tested by their respective characteristic properties and their presence in nitric acid can thus be proved. The formation of water proves the presence of hydrogen in HNO_3.. The presence of hydrogen in nitric acid is also confirmed by the reaction of magnesium with dilute HNO_3, when hydrogen is evolved. Magnesium does not react with cold water ;

$$Mg+2HNO_3=Mg(NO_3)_2+H_2.$$

(5) *Nitric acid is a very powerful oxidising agent*, particularly when hot and concentrated and displays a wide range of oxidising actions, the acid it self being reduced to oxides of nitrogen.

(a) Hot and concentrated acid oxidises the various non-metals like C, Si, P, S, I etc. either to their oxides or oxy-acids.

$$C+4HNO_3=CO_2+4NO_2+2H_2O$$
$$Si+4HNO_3=SiO_2+4NO_2+2H_2O$$
$$4P+10HNO_3+H_2O=4H_3PO_4+5NO+5NO_2$$
$$S+2HNO_3=H_2SO_4+2NO$$
$$3I_2+10HNO_3=6HIO_3+10NO+2H_2O.$$

Nitric acid has no action on Cl_2, Br_2 and N_2.

(b) Many a compound are readily oxidised by nitric acid. It oxidises SO_2 to H_2SO_4, ferrous sulphate to ferric sulphate.

Iodine, Bromine, sulphur, are set free from iodides, bromides and sulphides by nitric acid.

$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2$

$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO4)_3 + 2NO + 4H_2O$

$6KI + 8HNO_3 = 6KNO_3 + 2NO + 4H_2O + 3I_2$

$6KBr + + 8HNO_3 = 6KNO_3 + 2NO + 4H_2O + 3Br_2$

$3H_2S + 2HNO_3 = 2NO + 3S + 4H_2O$

(c) Hot concentrated nitric acid reacts with concentrated hydrochlorie acid, yielding chlorine and nitrosyl chloride.

$$3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O$$

A mixture of 3 volumes of concentrated hydrochloric acid and 1 volume of concentrated nitric acid is called *aqua regia*, it dissolves gold and platinum which are not attacked by concentrated acids. The action is due to the nascent chlorine formed in the reaction.

$$Au + 4HCl + HNO_3 = HAuCl_4 + NO + 2H_2O$$

(6) A mixture of concentrated nitric acid and sulphurie acid is nsed in the nitration of aromatic compounds, to yield the nitro-derivatives.

$$C_6H_6(\text{Benzene}) + HNO_3 = C_6H_5NO_2 + H_2O$$
(nitro benzene)

(7) *Reaction with metals* : Excepting a few noble metals, like gold, platinum, rhodium, iridium, nitric acid attacks most of the metals. The action of nitric acid on metals involves complicated reaction. This is presumably dne to the dual role of nitric acid as an acid and as an oxidising agent and as such, nitrates of the metals are formed, the acid is reduced to oxides of nitrogen, nitrogen, or even to ammonia. The degree of reduction depends on the strength of the acid, nature of the metal and temperature. Concentrated acid usually gives NO_2 especially at high temperatures. With dilute acid, nitric oxide (NO) and nitrous oxide (N_2O) are formed. With some metals like zinc, very dilute nitric acid may be reduced to ammonia, which with excess acid forms ammonium nitrate. But there are certain exceptions : (i) with dilute HNO_3, magnesium and manganese form hydrogen instead of oxides of nitrogen, (ii) tin and antimony are converted into their oxides and (iii) iron and aluminium become passive by concentrated nitric acid.

Reactions of nitric acid with some common metals are given below :—

Metal	Condition of reaction	Reaction
a) **Copper**	(i) Hot conc. acid,	(i) $Cu+4HNO_3=Cu(NO_3)_2$ $+2NO_2+2H_2O$
	(ii) Cold. moderately conc. acid (1 : 1)	(ii) $3Cu+8HNO_3=3Cu(NO_3)_2$ $+2NO+4H_2O$
	(iii) Cold, dilute acid	(iii) $4Cu+10HNO_3=4Cu(NO_3)_2$ $+N_2O+5H_2O$
b) **Zinc**	(i) Hot conc. acid,	(i) $Zn+4HNO_3=Zn(NO_3)_2$ $+2NO_2+2H_2O$
	(ii) Cold dilute acid :	(ii) $3Zn+8HNO_3=3Zn(NO_3)_2$ $+2NO+4H_2O$
	(iii) Cold, very dilute acid	(iii) $4Zu+10HNO_3=4Zn(NO_3)_2$ $+N_2O+5H_2O$ $4Zu+10HNO_3=4Zn(NO_3)_2$ $+3H_2O+NH_4NO_3$
c) **Mercury**	(i) Hot conc. acid	(i) $Hg+4HNO_3=Hg(NO_3)_2$ $+2NO_2+2H_2O$
	(ii) Cold dilute acid	(ii) $3Hg+8HNO_3=3Hg(NO_3)_2$ $+2NO+4H_2O$ $6Hg+8HNO_3=3Hg_2(NO_3)_2$ (excess). $+2NO+4H_2O$
d) **Iron**	(i) Hot, fairly conc. acid	(i) $Fe+4HNO_1)_3=Fe(NO_3)_3$ $+NO+2H_2O$
	(ii) Cold dil acid	(ii) $4Fe+10HNO=4Fe(NO_3)_2$ $+NH_4NO_3+3H_2O$
	(iii) Conc. or fumic acid	(iii) Metal does not dissolve and is rendered passive due to the formation of a film of oxide on its surface which protects the metal from further action of the acid.

Metal	Condition of reaction	Reaction
e) **Silver**	(i) Hot dil acid	(i) $Ag+2HNO_3=AgNO_3+H_2O+NO_2$
f) **Tin**	(i) Cold dil acid	(i) $4Sn+10HNO_3=4Sn(NO_3)_2+3H_2O+NH_4NO_3$
	(ii) Hot conc. acid	(ii) $5Sn+20HNO_3=H_2Sn_5O_{11}, 4H_2O+20NO_2+5H_2O$ metastannic acid, $H_2Sn_5O_{11}, 4H_2O$ decomposing by heat into tin dioxide and water.
g) Magnesium	very dil. acid	$Mg+2HNO_3=Mg(NO_3)_2+H_2$
h) Manganese		$Mn+2HNO_3=Mn(NO_3)_2+H_2$

The mechanism of reduction of nitric acid by metals to give different products may be explained by assuming that nascent hydrogen is first formed which then reduces the excess of nitric acid into different oxides of nitrogen at different concentrations. The theory explains the action of metals which are more electropositive than hydrogen. The action of zinc upon strong nitric acid can be explained thus :—

$$\begin{aligned}&Zn+2HNO_3=Zn(NO_3)_2+2H\\&2HNO_3+2H=2NO_2+2H_2O\\\hline&Zn+4HNO_3=Zn(NO_3)_2+2NO_2+2H_2O\end{aligned}$$

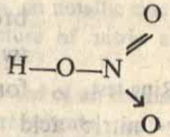
But in case of metals less electropositive than hydrogen, it is suggested that initially the metal is oxidised to its oxide which then dissolves in the acid The action of copper on cold dilute acid may be explained thus :—

$$\begin{aligned}&3Cu+2HNO_3=3CuO+2NO+H_2O\\&3CuO+6HNO_3=3H_2O+3Cu(NO_3)_2\\\hline&3Cu+8HNO_3=3Cu(NO_3)_2+2NO+4H_2O.\end{aligned}$$

24·13. Uses of Nitric acid :—Because of its diverse application in industry, nitric acid is the most important compound of nitrogen. Besides its uses in the laboratory, nitric acid finds application

(i) in large quantities for the manufacture of some nitrogen fertitisers like NH_4NO_3, $Ca(NO_3)_2$ etc. (ii) in the production of explosives such as dynamite, gun-cotton, T. N. T., picric acid, nitrocelluloses etc. (iii) in the manufacture of sulphuric acid by the chamber process, (iv) in the manufacture of celluloid, artificial silk, dyestuff etc., (v) in the "pickling" or cleaning of metals before electroplating.

Nitric Acid has the structural formula :



24·14. Nitrates :—The salts of nitric acid are called nitrates, which are prepared by the action of nitric acid on the metals, metal oxides or metallic carbonates. Nitric acid being monobasic, it produces only normal salts.

$$3Cu+8HNO_3=3Cu(NO_3)_2+2NO+4H_2O$$
$$CaCO_3+2HNO_3=Ca(NO_3)_2+CO_2+H_2O$$

The nitrates are obtained as crystalline solids and all nitrates are soluble in water. The nitrates of alkali metals give off oxygen on heating and are converted into nitrites, whereas the nitrates of other metals decompose on heating giving their oxides and generally NO_2 and oxygen.

$$2NaNO_3=2NaNO_2+O_2$$
$$2Pb(NO_3)_2=2PbO+4NO_2+O_2$$

Ammonium nitrate on heating gives nitrous oxide

$$NH_4NO_3=N_2O+2H_2O$$

Potassium nitrate, also called nitre, is an important ingredient of gunpowder. Calcium nitrate and ammonium nitrate are used as fertilisers.

24·15. Tests for nitric acid or nitrates :

(i) When nitric acid or a nitrate is warmed with conc H_2SO_4 and Cu-turnings, reddish brown fumes of NO_2 are evolved. (ii) A rose red colour is produced when a nitrate or nitric acid is added to a soluion of brucine in conc. H_2SO_4. (iii) Nitric acid or nitrates respond ring test. This is done as follows. A freshly prepared solution of ferrous sulphate is added to a cold dilute solution of a nitrate or nitric acid taken in a test tube. Then conc. H_2SO_4 is poured carefully by the side of the test tube so as to form a heavy layer at the bottom. A brown ring is formed at the junction of the two liquid layers in the test tube, due to the formation of $Fe(NO)SO_4$ (Fig 24.11). (iv) A nitrate or nitric acid when heated with Zn dust and concentrated NaOH solution gives off ammonia gas.

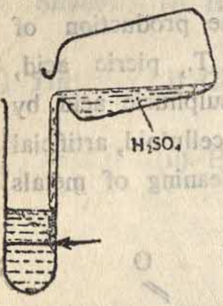


Fig 24·11 Ring test

$$NaNO_3+4Zn+7NaOH=NH_3+4Zn(ONa)_2+2H_2O.$$

Exercise—24

1. a) Give the names and formula of the five oxides of nitrogen, stating the oxidation number of nitrogen in these compounds.

b) Three cylinders are given to you full of colourless gases which may be either oxygen, nitrous oxide or nitric oxide. How will you identify them ?

2. Describe the preparation of pure sample of nitrous oxide in the laboratory In what respect does nitrous oxide differ from oxygen ? How has its formula been arrived at ? Why it is called 'laughing gas' ?

3. How would you prepare pure nitric oxide and discuss its important properties. How has the formula of the gas been established ? What happens when the gas is slowly passed for sometime into a jar of air confined over water ?

4. (a) Give at least three arguments to establish that air is a mixture of oxygen and nitrogen but nitric oxide is a compound of the two.

(b) Why does nitrous oxide support combustion better than air ?

5. Give an account of the preparation of nitrogen tetroxide. What is the effect of heat on this substance ? How it reacts with water and alkalis ? Suggest experiments to prove its oxidising power.

6. (a) How would you obtain a nitrite ? Mention the important properties of a nitrous acid solution.

(b) How are nitrites and nitrates identified ?

(c) nitrous acid readily passes into nitric acid and nitric oxide. Represent the change by a chemical equation. Why is it called a disproportionation reaction ?

7. (a) Give with sketch, a description of the preparation of nitric acid in the laboratory. How may the nitrogen present in nitric acid be converted into (i) ammonia, (ii) nitrous oxide, (iii) nitric oxide, and (iv) free nitrogen.

(b) How would you prove that nitric acid contains nitrogen, hydrogen and oxygen ?

8. How does nitric acid react with, (i) ferrous sulphate solution, (ii) H_2S gas, (iii) benzene, (iv) hydrochloric acid, (v) phosphorus pertoxide, (vi) magnesium, (vii) chorcoal (viii) Iodine, (ix) gold coin.

Give the conditions and the equations of the reactions.

9. Discuss the action of nitric acid, with conditions, on nutallic zinc and iron.

10, Give an out line of the method of manufacture of nitric acid from ammonia, What are the important uses of nitric acid ?

11. Nitric acid shows the Properties both of an acid and of an oxidising agent. —Illustrate, What gases are produced when ammonium nitrate, sodium nitrate and lead nitrate are separately heated ?

12. How would you prepare from sodium nitrate (i) concentrated nitric, acid, (ii) a dilurre solution of nitrous acid ? Compare then actions when treated with (a) ferous sulphate, (b) potassium iodide, (c) hydrogen sulphide and (d) potassium permanganate.

13. (a) How can you obtain ammonia from nitric acid and vice versa ?

(b) Explain why zinc produces hydrogen when acted on by dilute sulphurif acid but it does not produce hydrogen when acted on by nitric acid.

(c) Why H_2S is not prepared by the action of nitric acid on ferrous sulphide ?

14. (a) How much chile saltpetre will be required to produce 6·3 tons of nitric acid (Na = 23) ?

(b) What volume of nitric oxide at N. T. P. can be produced the action of nitric acid on 12.7 gms of copper ? (Cu = 63·5)

[Ans :—(a) 8·5 tons , (b) 2·99 litres]

15. Explain what happens when—

(a) sodium bromide is added to concentrated nitric acid,

(b) acidified potassium nitrite solution and potassium iodide solution are mixed.

(c) nitrus acid solution is heated with ammonium chloride.

(d) sodium nitrate solution is heated with zinc dust and caustic soda and the evoloved gas is led into sulphuric acid.

(e) Strong sulphuric acid is poured carefully into ferrous sulphate dissolved in cold dilute nitric acid.

CHAPTER XXV

CARBON

Atomic number 6, Atomic weight 12·00 density (diamond 3·51, graphite 2·25), Electronic configuration : $1s^2 2s^2 2p^2$.

The element carbon stands for the chief source of energy of the world. Although it constitutes about 0·03 percent of the earth's crust, more compounds of carbon are known than all the other compounds put together. Carbon is an important constituent in all kinds of fuel, food, clothing, dyes, drugs, explosives and is one of the basic elements in all living matter.

25·1. Occurrence :—In the free state, pure carbon occurs in nature as diamond and graphite which are highly crystalline. Coal is also largely carbon mixed with volatile impurities. In combination carbon occurs in various compounds which are quite widespread. Of the compounds of carbon, the most abundant are petroleum, limestone and chalk. Air contains carbon dioxide (about 4 volumes in 10,000). An essential constituent of all animal and vegetable bodies, it is found as carbohydrates, proteins and host of other organic compounds·

25·2. Allotropy of Carbon :—Carbon exhibits allotropy and exists in several allotropic forms. The different allotropes of carbon are : (i) crystalline which includes diamond and graphite ; and (ii) amorphous which includes various charcoals (wood charcoal, animal charcoal etc.), lampblack or soot, gas carbon and coke.

Graphite is the stablest form of carbon. X-ray studies has revealed that charcoal and many other varieties of so-called amorphous carbon consist of microcrystals of graphite.

These different forms of carbon are quite distinct outwardly and their physical characteristics also differ. But equal weights of the different forms when burnt in oxygen separately, produce always carbondioxide, which can be absorbed in previously weighed caustic-potash tubes, when identical weights of carbondioxide are obtained in all cases. This confirms the identity of different allotropes of carbon.

25 3. Crystalline Allotropes of Carbon :—

(a) **Diamond** :—In nature dimond occurs in south Africa and some other African States, Brazil, Borneo, the Ural mountains, New South Wales and at Golconda in India. South African mines alone supply over 90% of the World's diamond.

Diamond usually occurs as small crystals embedded in rocks. The rocks are crushed and their suspension in water is led over slopping greased tables. The diamond crystals, being very heavy sink and stick to the greased floor of the table from where they are collected. Indian small diamonds are generally found in river gravels and alluvial deposits and also extracted in the same way

Diamond, which is used as gem-stone, is rated in carats (1 carat = 0·200 gms). Most diamonds are small, but the largest piece of diamond (~ $1\frac{1}{2}$ lb) known as Cullinan diamond, was discovered in the South African mine at Kimberley in 1905. Some famous diamonds are Kohinoor (106 carats), Cullinan (3032 carats), Pitt (136·25 carats), and Hope (44·5 carats).

Properties :—(i) Pure diamond is a colourless lustrous transparent substance. It appears in octahedral crystals. The refractive index (2·42) and the dispersive power of diamond are abnormally high, so that white light passing through a diamond gives rise to brilliant play of colours. On account of this property diamonds are magnificent gemstones. In order to produce the most brilliant sparkling effect, natural diamonds are cut into geometrical forms by grinding. Diamonds, unlike all less costly substitutes, are transparent to X-rays. Less valuable diamonds are tinted yellow, or less frequently pink, green or blue. Some varieties, known as carbonado or bort are opaque and black—these have no value as gems but are used in cutting and polishing.

(ii) It is the densest form of carbon with a specific gravity 3·52 and is the hardest substance known. It is not scratched by any substance (except boron carbide B_4C). It is a bad conductor of heat and electricity.

(iii) Diamond is chemically very inert and is not attacked by acids, alkalis or fused potassium chlorate or by chlorine. It may however burns in oxygen and fluorine giving carbondioxide and carbon tetra-fluoride respectively.

$$C+O_2=CO_2\ (800°C) \qquad C+2F_2=CF_4\ (700°C).$$

(iv) Diamond dissolves in molten iron. In absence of air, if diamond is heated to a temperature aboue 1000°C, it slowly changes into graphite.

Artifical preparation of Diamond : It has been shown experimentally as well as from theoretical calculations that diamond is in equilibrium with graphite at 2000°C and a pressure of 30,000 atmospheres. Attempts were made to prepare artificial diamond by subjecting graphite powder under high pressure at a high temperature. In 1893 Moissan claimed to have isolated minute crystals of diamond by dissolving sugar charcoal in molten iron at 4000°C in an electric arc furnace and then suddenly chilling the solution by immersion in molten lead (327°C). Iron was dissolved away by hydrochloric acid, when the small pieces of diamond were obtained. Recently the General Electric Company of New York has prepared small artifical diamond by putting graphite at 3000°C at a pressure of 53000 atm. for several hours. The artificially prepared diamonds are however, more costly than natural diamonds.

Uses :—Diamond is used as a gem-stone. The value of the gem depends upon its lustre and transparency. On account of its extreme hardness, diamond is used for cutting glass and other diamonds. Carbonado or bort, being less valuable are usually used for drilling rocks.

(b) **Graphite** :—Graphite, which is also known as *plumbago* or *black lead* is found in large deposits iu Ceylon, Siberia, U.S.A,, Italy, Bohemia and elsewhere. Deposits of graphite have been found in Sikkim near W. Bengal and also in Trivancore.

Properties :—(i) Graphite is dark grey in colour with a metallic lustre, relatively soft and a density of 2.25 gm/c.c. Graphite is formed of hexagonal crystals arranged in flakes and these flakes slide over one another. It is opaque, has a greasy touch and easily marks paper, hence the use of graphite in the so called lead pencils. Though a non-metal, it is a good conductor of heat and electricity.

(ii) Compared to diamond, graphite is more reactive. Thus it burns in air at 700°C to produce carbondioxide and reacts with fluorine at 500°C to form CF_4. When heated with a mixture of concentrated sulphuric and nitric acids and a little potasium chlorate, graphite is converted into a yellow insoluble solid known as graphitic acid or oxide. In this condition diamond is unattacked and amorphous carbon forms soluble brown mass. Though unattacked by dilute acids, caustic alkalis or chlorine, it is slowly oxidised to CO_2 by chromic acid and to CO by fused sodium carbonate.

Artificial Graphite :—Because of its high demand for various purposes, graphite is now manufactured artificially by *Acheson's proeess.* An intimate mixture of sand and powdered petroleum coke is strongly heated electrically in a furnace made of fireproof bricks. (Fig 25.1). Electricity is led in the mixture through carbon rods embedded in the mass and heating is continued for about 30 hours at a temperature above 2500°C. Sand (silicon dioxide) first reacts with carbon forming silicon carbide, which is subsequently decomposed at very high temperature into graphite and silicon. Silicon vaporises off and pure graphite is left in the furnace.

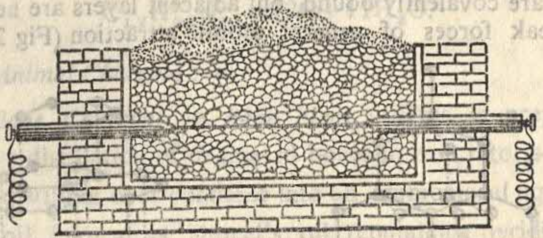


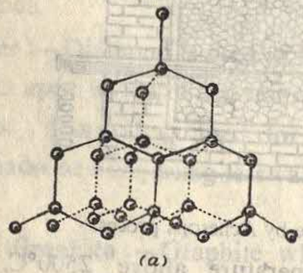
Fig. 25·1. Graphite by Achesons process

$$SiO_2+C=SiC+2CO \quad SiC=Si+C.$$

Uses :—(i) As graphite marks paper, it is used for making "lead pencils". Lead pencil do not have any lead in it. (ii) As it is a good conductor of electricity, graphite is used as electrodes and heating elements in electric furnaces, and for coating articles of non-conducting materials meant for electrotypings, (iii) colloidal graphite as a suspension in oil is used in lubricating machinery, (iv) Mixed with clay, it is used in making plumbago crucibles which combine refractory properties with thermal conductivity. (v) Very pure graphite serves as a moderator in atomic reactors.

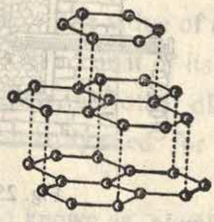
25·4. Structure of diamond and graphite :—The difference in crystal structures of diamond and graphite are reflected in their different properties. The diamond crystal is built up of giant three dimensional molecules with tetrahedral arrangement of carbon atoms —each atom is bound covalently by electron pairs to four other atoms around it at the corners of a regular tetrahedron (Fig 25.2) The forces acting between the atoms are very strong, the entire crystal being a single huge carbon molecule. The very compact uniformly-bound structure of the diamond accounts for its extreme hardness and for its lack of chemical reactivity.

The structure of graphite is different. The crystal is formed of layers of carbon atoms disposed in hexagonal rings. The atoms in each layer are covalently bound, but adjacent layers are held together by the weak forces of general atomic attraction (Fig 25.3). The structure of graphite crystal, therefore, consists of two-dimentional molecules piles on one another relatively loosely. The ability of the layers to slip over one another accounts for the soft flaky nature of graphite, and for its value as lubricant.



(a) diamond

Fig. 25·2. Structure of diamond



(b) graphite

Fig. 25·3. structure of graphite

25 5. Amorphous Carbon :—There are several varieties of so-called amorphous carbon, a brief description of these varieties is given here.

1. Charcoal : There are several types of charcoal, depending upon its source of which wood charcoal, animal charcoal and sugar charcoal are important.

(*a*) *Wood Charcoal* :—This is obtained by the dry distillation of wood in extremely heated Iron retots from which air is excluded. The volalile products of decomposition escape as *wood gas* by an exit pipe, the black solid residue left in the retort is the *wood charcoal.* The wood-gas is allowed to cool in a tank where a liquid tar (wood-tar) and an aqueous distillate, named *pyroligneous acid*, separate. This pyroligneous acid is valuable as it contains acetic acid, methyl alcohol and acetone.

(*b*) *Sugar Charcoal* :—This is the purest from of amorphous carbon and is prepared by the *destructive distillation* of sugar or by charring sugar with concentrated H_2SO_4. The product is then heated to 1000°C in a stream of chlorine gas to remove the residual combined hydrogen as hydrogen chloride. It is next washed with water and dried in a current of hydrogen to remove chlorine.

$$C_{12}H_{22}O_{11} = 12C + 11H_2O.$$

(*c*) *Animal Charcoal* :—

(*i*) *Bone Charcoal or bone black* :—This is prepared by the destructive distillation of degreased bones in iron retorts—the volatile products distilling over condense into an ammoniacal aqueous liquid and an oil known as Dippel's oil (containing pyridine and other organic bases). The black residue left in the retort is the animal charcoal. It is also called *Bone Black* and contains only about 10% of carbon and the rest is mainly calcium phosphate and calcium carbonate. The calcium salts are removed by dissolving with hydrochloric acid and the charcoal left is known as *ivory black.*

(*ii*) *Blood Charcoal*—The destructive distillation of animal blood also gives *blood Charcoal* in a similar way.

Active Charcoal :—As ordinarily prepared, charcoal is usually covered with a thin layer of comparatively inactive graphitic material which reduces to a large extent its adsorptive power. Active charcoal is prepared by heating wood charcoal to about 1000°C in a current of steam which destroys the graphitic layer. Thus its adsorptive capacity is tremendously increased. Coconut shells on carbonisation give a very active form of charcoal.

Propertiss of Charcoal :—(i) Charcoal is a black, soft and a porous substance. Its density varies between 1.4~1·9 gm/cc; but its density is reduced to about 0·2 by air enclosed in its pores, and hence charcoal floats on water. It is a bad conductor of heat and electricity.

(ii) Because of its porosity charcoal readily adsorbs gases. Absorbed gases are released from charcoal by heating. It also adsorbs dissolved substances from a solution. For example, if a dilute solution of litmus is boiled with animal charcoal the litmus is adsorbed and the solution is rendered colourless.

(iii) Charcoal ignites in oxygen at about 400°C. At high temperature, it combines with sulphur to form carbon disulphide, which is an endothermic compound.

$$C+2S=CS_2\ ;\ \Delta H=+26{,}000\ \text{Cal.}$$

It ignites spontaneously in fluorine, yielding CF_4, while other halogens have no action on charcoal.

(iv) Charcoal is not attacked by alkalis, hydrochloric acid, but hot conceutrated H_2SO_4 and HNO_3 acids oxidise charcoal to carbondioxide.

$$C+2H_2SO_4=CO_2+2H_2O+2SO_2$$

$$C+4HNO_3=CO_2+2H_2O+4NO_2$$

(v) Charcoal is a good reducing agent at high temperaturs. It reduces heated metallic oxides such as CuO, PbO, Fe_2O_3 ZnO, etc., to the respective metals. Red hot charcoal reduces steam to hydrogen and carbondioxide to carbon monoxide.

$$ZnO+C=Zn+CO \qquad H_2O+C=H_2+CO$$

$$CuO+C=Cu+CO \qquad CO_2+C=2CO.$$

(vi) Small amount of methane is formed by combination of carbon with hydrogen at high temperature and pressure. Acetylene is formed when a spark is passed between carbon electrodes in hydrogen. When heated with silicon in an electric furnace, it gives silicon carbide or carborandum. Coke heated with lime in electric furnace gives calcium carbide.

$$CaO + 3C = CaC_2 + CO.$$

2. **Lamp black** :—In a limitted supply of air, carbon-rich organic substance, such as kerosine, petroleum, turpentine etc. are allowed to burn. They burn with a smoky flame and the smoke is allowed to enter into a cold chamber where carbon is deposited as a deep black mass called *lamb black or soot*. It is a bad conduetor of heat and electricity.

3. **Coke and Gas-Carbon** :—These are the by-products of the coal-gas industry. *Coke* is obtained as a porous non-volatile solid containing about 85 per cent. of carbon which remains as a residue in the retort after the volatile matter has been driven off from coal by dry distillation. If the distillation is carried out at high temperature, the product is called hard coke, which is suitable for metallurgical purposes. If the distillation is effected at lower temperature, it is soft coke, which is used mostly for domestic purposes. Coke is a bad conductor of heat and electricity.

Gas-Carbon is a hard deposit of almost pure carbon formed on the hot walls of the retorts by the thermal decomposition of hydrocarbons liberated from the coal during the manufacture of coal gas. It is a good conductor of heat and electricity.

Uses of carbon :—The use of diamond and graphite have been mentioned earlier. The uses of the amorphous varietis of carbon are given below :—

(i) Wood charcoal is used as a fuel, as a reducing agent and in filter-beds for purification of water. It is used in the manufacture of gun-powder. Activated charcoal is used as adsorbent in gas-mask.

(ii) Animal charcoal is used in refining of sugar syrups. Ivory black is an important black pigment.

(ii) Lamp black in the fiinely divided state is used in making printer's ink, shoe-polish and as a useful component of rubber in the rubber industry.

(iv) Coke is used as a solid fuel and as a reducing agent in the metallurgy of iron and certain other metals. It is also used in the production of gaseous fuel like water-gas, producer gas.

(v) Gas carbon is used as electrodes in arc lights and in some electric batteries.

25·6. Coal :—Coal was formerly regarded as a variety of carbon but actually it is not. Coal is a carbonaceous mineral of vegetable origin. This may be regarded as the final product of the slow decomposition undergone by the vast primaeval forests submerged under the earth's surface in remote past and subjected to high pressure and temperature. The successive stages in the transformation of vegetable matter into coal are apparently represented by peat (60%C), lignite (67%C), bituminous coal (88·4%C) and anthracite (94%C). Each step of conversion is followed by an increase in the percentage of carbon in the residue with the corresponding increase in calorifie value. The ash left on burning coal is derived from the vegetable and mineral matters present in coal.

Coal is extensively used as a fuel and in the manufacture Coal-gas and liquid fuels.

Comparison of the different allotropic forms of carbon.

Property	Diamond	Graphite	Amorphous Carbon
(1) Colour and appearance.	Colourless, transparent, lustrous crystalline solid	Greyish black, opaque crystals with metallic lusture.	Black amorphous solids
(2) Density (gm/cc) & O Hardness···	3·52, hardest substance known	2·25, soft, greasy to toueh.	charcoal 1·4 to 1·9 gas, carbon 2·25, charcoal soft and porous ; coke hard of soft ; gas carbon hard.
(3) Electrical conductivity···	Bad conductor	Good conductor	Gas carbon good conductor, the rest are bad conductors
(4) Effect of heat···	Changes to graphite at 1800°C	Stable form at high temperature	Changes to graphite at high temperature
(5) Burns with flame in oxygen ··	Produces CO_2 at 800 - 850°C, high ignition temperature	Produce CO_2 at 700°C	CO_2 at 400°C (wood charcoal), low ignition temperature.
(6) Reaction with fluorine···	forms CF_4 at 700°C	froms CF_4 at 500°C	Ignites spontanleously to CF_4

OXIDES OF CARBON

Carbon forms two important gaseous oxides : (i) Carbon monoxide and (ii) Carbon dioxide.

25·6. Carbon Monoxide, CO :—Carbon monoixide is hardly found in nature, small amount occurs in volcanic gases. It occurs in coal-gas and water gas. It is also present over burning coal or charcoal and in the exhaust gases of motor-engines. It originates from incomplete combustion of carbon in a limited supply of air.

Preparation :—(i) *Loboratory Method* :—Carbon monoxide is generally prepared in the laboratory by abstracting the elements of water from formic acid or oxalic acid with the help of concentrated sulphuric acid. H_2SO_4 acts as a dehydrating agent.

Concentrated sulphuric acid is taken in a flask and heated to about 100°C. The flask is fitted with a dropping funnel containing formic acid and a delivery tube (Fig 25.4). Formic acid is allowed to fall on hot concentrated H_2SO_4 drop by drop when carbon monoxide is evolved. The gas coming out of the delivery tube may contain traces of SO_2 and CO_2 formed by the reduction of sulphuric acid :

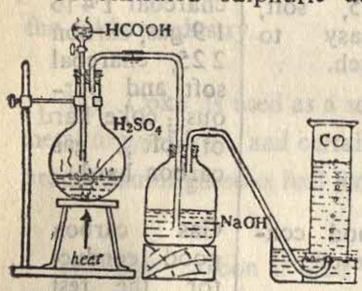


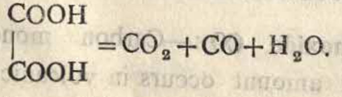
Fig. 25·4. Preparation of CO

$$H_2SO_4 + CO = H_2O + SO_2 + CO_2.$$

To remove these, the gas is washed with caustic soda solution and then collected by the displacement of water. The gas may also be obtained by heating sodium formate with concentrated sulphuric acid :

$$HCOOH = CO + H_2O.$$

Equimolar mixture of carbon monoxide and carbon dioxide is obtained when a mixture of powdered oxalic acid and conc. sulphuric acid is heated in a flask. By passing the produced gas through strong caustic soda solution, carbon dioxide is removed and the undissolved carbon monoxide is collected over water. It may be dried with phosphorus pentoxide and collected over mercury.



$$\begin{array}{l}COOH\\ |\\ COOH\end{array} = CO_2 + CO + H_2O.$$

(ii) Pure carbon monoxide is usually prepared by heating potassium ferrocyanide with conc. sulphuric acid.

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO.$$

(iii) A pure sample of carbon monoxide may be obtained by heating nickel carbonyl, $[Ni(CO)_4]$ at 180°C :

$$Ni(CO)_4 \xrightarrow{\text{heat}} Ni + 4CO.$$

(iv) Carbon monoxide may be formed by the partial oxidation of carbon by heating in a limited supphy of air or oxygen : $2C + O_2 = 2CO$. It is also prepared by passing CO_2 over red hot carbon (about 1000°C) : $CO_2 + C = 2CO$ or by heating charcoal with oxides of Zinc or Iron or with chalk :

$$ZnO + C = CO + Zn \; ; \; CaCO_3 + C = CaO + 2CO.$$

(v) When steam is passed over white-hot coke (1000°C) a mixture of carbon monoxide and hydrogen, called *water gas*, is obtained. The reaction is endothermic.

$$C + H_2O = \underset{\text{(water gas)}}{CO + H_2} \; ; \quad \Delta H = +29000 \text{ cal.}$$

When air is passed over white hot coke (1000°C), the mixture of carbon monoxide and nitrogen produced, is called *producer-gas*. The reaction is exothermic :

$$C + \text{air} \rightarrow \underset{\text{(producer gas)}}{CO + N_2} \; ; \quad \Delta H = -29000 \text{ cal.}$$

Carbon monoxide is not prepared in a pure state for commercial use ; water-gas or producer-gas are used instead of pure carbon monoxide.

25·7. Properties of Carbon monoxide : (i) Carbon monoxide is a colourless gas with a peculiar faint smell. It is slightly soluble in water, but it is readily absorbed by ammoniacal or hydrochloric acid solution of cuprous chloride, with the formation of the compound $[CuCl. CO. 2H_2O]$.

(ii) Carbon monoxide is very poisonous. Inhaling air containing 0·6% carbon monoxide may prove fatal. Its poisoning effect is due to the fact that it combines with haemoglobin and thereby blood looses its capacity of carrying oxygen. The lack of oxygen leads to death. This explains why it is dangerous to burn coke in chambers insufficiently ventilated.

(iii) Carbon monoxide is not a supporter of combustion, but it burns in air or oxygen with a blue flame producing carbondioxide :

$$2CO+O_2=2CO_2.$$

(iv) It is a neutral oxide. It does not react wlth an acid or an alkali. But under pressure at 200°C, it combines with concentrated NaOH forming sodium formate :

$$NaOH+CO=HCOONa.$$

(v) An unsaturated compound, it undergoes additive reactions : it combines directly with chlorine in sunlight giving carbonyl chloride also called phosgene, $CO+Cl_2=COCl_2$. With sulphur vapour it forms carbonyl sulphide :

$$CO+S=COS.$$

Carbon monoxide reacts with many metals like. iron, cobalt, nickel etc. at slightly elevated temperature to form metallic carbonyls which are usually volatile liquids :

$$Ni+4CO=Ni(CO)_4\ ;\ Fe+5CO=Fe(CO)_5.$$

(vi) Carbon monoxide is a reducing agent. It reduces the oxide of such metals as lead, copper and iron at red-heat, but it will reduce neither aluminium oxide nor the oxides of other metals which stand high in the electrochemical series.

$$CuO+CO=Cu+CO_2\ ;\ Fe_2O_3+3CO=2Fe+3CO_2.$$

At room temperature cardon monoxide reduces Fehling's solution to cuprous oxide, and ammoniacal silver nitrate solution to silver, at 90°C, it reduces iodine pentoxide to iodine, thus :

$$I_2O_5+5CO=I_2+5CO_2.$$

Carbon monoxide reduces steam in presence of mixed catalyst $(Fe_2O_3+Cr_2O_3)$.

$$CO+H_2O=CO_2+H_2$$

(vii) The mixture of carbon monoxide and hydrogen when passed over the catalyst (Cr_2O_3+ZnO) yields methyl alcohol at about 350°C.

$$CO+2H_2\xrightarrow[350°C]{Cr_2O_3+ZnO}CH_3OH.$$

Uses :—As a constituent of water gas and producer gas, carbon monoxide is used as a fuel. It is required in the synthesis of methyl alcohol. It is also used in the extraction of nickel and sometimes used as a reducing agent in metallurgy.

Tests :—(i) Carbon monoxide burns with a bluish flame yielding carbon dioxide which turns lime water milky. (ii) Traces of carbon monoxide in air is detected by shaking with diluted blood and then examining its spectroscopically. If carbon monoxide is present, the blood would give a deep red precipitate with tanin solution whereas normal blood gives a light brown precipitate.

25·8. Composition of Carbon monoxide by Volume :—On combustion with oxygen carbon monoxide yields only carbon dioxide ; it therefore consists only of carbon and oxygen. A given volume of carbon monoxide and excess of oxygen are collected over mercury in a U-shapped eudiometer tube (Fig 25.5) and exploded. The explosion takes place with a contraction in volume (due to absorption of oxygen by carbon monoxide), which is equal to half the volume of carbon monoxide taken. There is a further contraction on absorption with caustic potash—this is due to carbon dioxide formed ; it is equal to the volume of carbon monoxide taken :

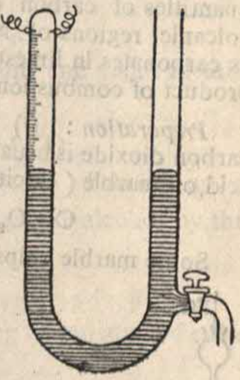


Fig. 25·5 Composition of Carbonmonoxide

$$C_xO_y+O_2\rightarrow CO_2.$$

Hence, 1 volume of carbon monoxide combines with half volume of oxygen to give 1 volume of carbon dioxide. But 1 volume of

CO_2 contains 1 volume of oxygen, of which one-half is derived from gaseous oxygen, so that the other half must be present in carbon monoxide. Hence carbon monoxide contains half its own volume of oxygen. i.e.

1 volume carbon monoxide cantains $\frac{1}{2}$ volume of oxygen so, by Avogadro's hypothesis,

1 molecule carbon monoxide contains $\frac{1}{2}$ molecule, i.e.
1 atom of oxygen.

Hence the formula is C_xO and the mol. wt. $= 12x+16$.

But the vapour density of carbon monoxide $= 14$.

$\therefore$ its molecular weight $= 14 \times 2 = 28$.

$\therefore$ $12x+16=28$ or, $x=1$.

So the molecular formula of carbon monoxide is CO. The molecular structure of carbon monoxide may be represented as $\overset{-}{C}\equiv\overset{+}{O}$ or $C\overset{\leftarrow}{=}O$

25·9. Carbon dioxide, CO_2 :—In the free state, carbon dioxide occurs in the atmosphere to the extent of 0·03 per cent. by volume. Carbon dioxide is also present in certain spring water. Large quantities of carbon dioxide are issued from the earth near the volcanic regions of Naples and Java. Carbon-dioxide also occurs as carbonates in limestone, marble, dolomite etc. It is the ultimate product of combustion of carbon and its compounds.

Preparation : (*i*) *Laboratory method* :—In the laboratory, carbon dioxide is usually prepared by the action of dilute hydrochloric acid on marble (calcium carbonate).

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

Some marble chips are taken in a Woulfe's bottle fitted with a thistle funnel and a delivery tube. Dilute hydrochloric acid is now added through the thistle funnel until its end is under the level of the acid. As soon as the acid comes in contact with the marble, quick effervescence takes place due to the evolution of carbon doxide. The gas comes out of the delivery tube and may be collected over water

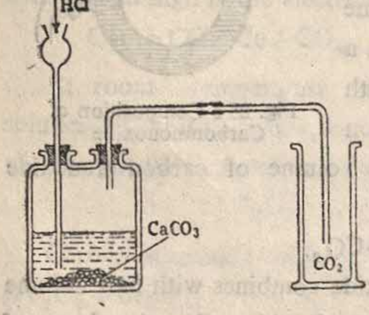


Fig. 25·6. Preparation of carbondioxide

(though it is some what soluble) or by the upward displacement of air, since it is 1½ times heavier than air (Fig. 25·6).

If pure and dry carbon dioxide is required, the gas is passed through water to free it from traces of HCl accompanying it and then through conc. H_2SO_4 to remove water vapour. It is finally collected over mercury.

In the preparation of carbon dioxide, dilute sulphuric acid is not used because of the formation of an insoluble layer of calcium sulphate on the marble which prevents further reaction.

For ready supply of the gas, kipp's apparatus is used, marble chips are placed in the middle globe and dilute hydrochloric acid in the upper globe of the apparatus.

Other carbonates also yield carbon dioxide when acted upon by dilute acids ; e.g.,

$$Na_2CO_3+2HCl=2NaCl+CO_2+H_2O$$

$$MgCO_3+H_2SO_4=MgSO_4+CO_2+H_2O$$

(ii) Pure carbon dioxide is sometimes prepared by heating sodium bicarbonate :

$$2NaHCO_3=Na_2CO_3+H_2O+CO_2.$$

The metallic carbonats, except those of barium and alkali metals, give off carbon dioxide when strongly heated.

$$MgCO_3=MgO+CO_2\ ;\ ZnCO_3=ZnO+CO_2.$$

(iii) On the *industrial Scale* : Carbondioxide is obtained as a by-product either in the fermentation of sugar to alcohol by the action of enzyme *zymase* :

$$C_6H_{12}O_6=2C_2H_3OH+2CO_2$$

or, in the manufacture quicklime by burning a mixture of coke and limestone in a limekiln.

$$CaCO_3=CaO+CO_2.$$

The gas can also be manufactured by burning coke in excess of air :

$$C+O_2=CO_2.$$

The carbon dioxide is separated from nitrogen and other gases by absorption in cold potassium carbonate solution, from which it is subsequently expelled by boiling :

$$K_2CO_3+CO_2+H_2O=2KHCO_3.$$

25·10. Properties of Carbondioxide :—(i) Carbondioxide is a colourless, odourless gas, one and half times heavier than air. Carbon dioxide is soluble in water, it is completely expelled from the solution on boiling. At ordinary temperature, water dissolves its own volume of carbon dioxide. Under high pressure, large amount of carbon dioxide may be dissolved as in aerated water like soda, lemonade, etc.

(ii) Its critical temperature is 31°C ; below this temperature it may be compressed to a liquid. If this liquid is allowed to evaporate rapidly in air, it solidifies to a white solid, carbon dioxide snow called *dry ice.* Solid carbon dioxide or dry ice under ordinary pressure sublimes, leaving no residue.

(iii) The gas is non-poisonous, but no living body can live in it because of suffocation.

(iv) carbon dioxide is neither combustible nor a supporter of combustion, and hence it is used as a fire extinguisher. But ignited Mg, Na or K burn in the gas with separation of carbon.

$$2Mg+CO_2=2MgO+C\ ;\ 4K+3CO_2=2K_2CO_3+C.$$

This reaction shows that carbon dioxide contains carbon.

(v) It is an acidic oxide and as such, combines with bases to form carbonates. Its aqueous solution is acidic due to the formation of unstable carbonic acid : $CO_2+H_2O=H_2CO_3$. So CO_2 is the anhydride of carbonic acid. Carbonic acid is known only in solution ; it does not exist in the pure state. But its salts are available in pure state. It is a weak dibasic acid and gives rise to two types of salts, carbonates and bicarbonates :

$$CaO+CO_2=CaCO_3\ ;\ Na_2O+CO_2=Na_2CO_3$$
$$2NaOH+CO_2=Na_2CO_3+H_2O$$
$$NaOH+CO_2=NaHCO_3$$

The reaction with lime-water is interesting. When CO_2 gas is bubbled through lime water, it turns milky due to the formation of white insoluble calcium carbonate :

$$Ca(OH)_2+CO_2=CaCO_3+H_2O.$$

But it the gas is passed in excess, the milkiness disappears due to the formation of calcium bicarbonate which is soluble in water :

$$CaCO_3+H_2O+CO_2=Ca(HCO_3)_2$$

If now the calcium bicarbonate solution be boiled, it again turns milky due to re-formation of the insoluble calcium carbonate.

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2$$

(vi) Carbon dioxide is a stable compound ; not more than 1% would decompose even when heated to 1600°C.

$$2CO_2 \rightleftharpoons 2CO + O_2.$$

carbon dioxide is reduced to carbon monoxide when passed over red-hot coke, or iron or zinc.

$$CO_2 + C = 2CO \ ; \ CO_2 + Zn = ZnO + CO.$$

(vii) carbon dioxide is absorbed by green plants in presence of sunlight and chlorophyll and is ultimately transformed into carbohydrates by interaction with moisture, oxygen being set free in the process, which is known as *photosynthesis.*

$$xCO_2 + xH_2O = (CH_2O)_x + xO_2.$$

Uses :—(i) carbon dioxide is used in the manufacture of sodium carbonate and urea.

(ii) Dry ice is extensively used as a refrigerant for preservation of meat, fish etc. and for ice-cream.

(iii) It is used in the preparation of aerated water such as lemonade in which CO_2 is kept dissolved under pressure.

(iv) It is also used as fire-extinguisher. A fire-extinguisher (Fig 25.7) consists of a metal casing B containing a concentrated solution of sodium carbonate, with a sealed glass bottle T of sulphuric acid inside. The bottle may be broken by rod attached to a knob H outside, when the acid comes in contact with the carbonate, carbon dioxide is generated which forces itself out through the nozzle N and is directed against the fire. It really forms a blanket over the fire and shuts of oxygen.

Tests :—(i) Carbon dioxide extinguishes a burning taper, (ii) Carbondioxide turns lime water milky which disappears with prolonged passing of the gas.

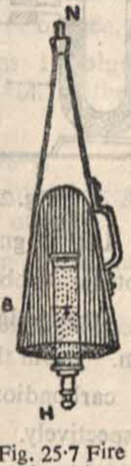


Fig. 25·7 Fire extinguisher

25·11. Composition of Carbon dioxide :—

(*a*) *Gravimetric Composition* :—The gravimetric composition of carbon dioxide is determined by passing a slow stream of oxygen over a weighed quantity of carbon heated in a combustion tube and weighing the carbon dioxide formed,

About 1 gm. of pure charcoal is accurately weighed in a porcelain boat and it is introduced in a hard—glass combustion tube one half of which is packed with granular copper oxide. (Fig. 25.8) A slow stream of pure and dry oxygen is passed through the combustion tube, while it is heated by a burner or in a furnace. The other end of the tube is fitted with a bubbler containing strong caustic potash solution, which is previously weighed. During heating charcoal is oxidised to carbon dioxide. Any trace of carbon monoxide formed would be transformed into dioxide by the copper oxide. The entire quantity of carbon dioxide would be absorbed in the potash bubbler which is again weighed after the experiment. Thus the weight of carbon dioxide formed is known.

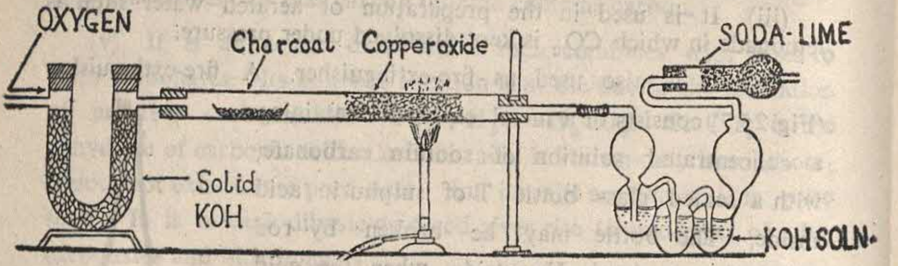


Fig. 25·8. Determination of gravimetric composition of CO_2.

Let x gm = weight of carbon and y gm = increase in weight of potash bubbler, which is weight of carbon dioxide formed. ∴ the weight of oxygen combined with x gm of carbon = (y – x) gm. From the actual data, the percentage of carbon and oxygen in carbondioxide has been calculated to be 27·27 and 72·73 respectively.

$$\therefore \frac{\text{the number of C atoms}}{\text{the number of O atoms}} = \frac{27{\cdot}27/12}{72{\cdot}73/16} = \frac{1}{2}.$$

So the empirical formula of carbon dioxide is CO_2, so its molecular formula is $(CO_2)_x$. $\therefore$ mol.wt.$=(12+32)x$, But the molecular weight of carbon dioxide is 44, its relative density being 22.

$$\therefore\ (12+32)x=44 \quad \therefore\ x=1.$$

$\therefore$ the molecular formula is CO_2.

(*b*) *Volumetric Composition* :—The volumetric composition of carbon dioxide is found by burning a piece of sugar charcoal in a confined volume of oxygen over mercury. the apparatus consists of a U-shapped eudiometer tube, one arm of which ends in a stoppered globe (Fig 25.9). Through the stopper enter two copper wires, one of which ends in a metal spoon. The spoon is connected to the other wire by a thin platinum spiral. In the spoon is placed a small amount of pure sugar charcoal. The bulb and a part of the limb is filled with oxygen at atmospheric pressure by the displacement of mercury, and the charcoal is ignited by passing electric current through the platinum spiral by joining the two wires to the terminals of a battery. Carbon is burnt into carbondioxide. After the reaction is over, the apparatus is allowed to cool to room temperature. It is found that mercury stands at the same level as before, i.e., there is no contraction or expansion in volume. This means that the carbon dioxide formed has the same volume as that of the oxygen used up. Hence carbon dioxide contains its own volume of oxygen.

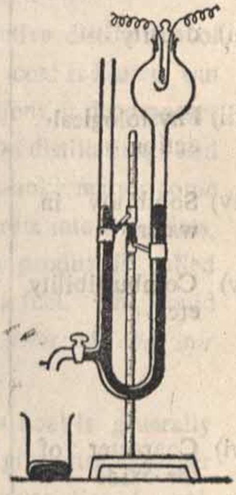


Fig. 25·9. Composition of carbondioxide

Therefore, 1 volume of carbon dioxide contains 1 volume of oxygen. Let n be the no. of molecules contain in 1 vol. of the gas, then, by Avogadro's hypothesis,

n molecules of carbon dioxide n molecules of oxygen,

or, 1 molecule of carbondioxide contains 1 molecule of oxygen,
i.e., 2 atom of oxygen.

Hence the formula of carbon-dioxide is C_xO_2 and the molecular weight$=12x+32$.

But the vapour density of the gas is found to be 22, hence, the molecular weight$=44$.

$$\therefore\ 12x+32=44 \quad \text{or} \quad x=1.$$

Therefore the formula of carbondioxide is CO_2.

The structure of carbondioxide is linear as the substance is non-polar. So it has the structure : $O=C=O$.

Comparison between carbon menoxide and carbon dioxide :

Properties	Carbon monoxide	Carbon dioxide
(i) Nature, colour, smell etc.…	Colourless gas, peculiar faint smell, liqufiable at very low temp. and high pressure.	Colourless, odourless gas, easily liquefiable under pressure.
(ii) density…	nearly as heavy as air	$1\frac{1}{2}$ times heavier than air
(iii) Physiological action…	Highly poisonous	Non-poisonous, but causes suffocation.
(iv) Solubility in water…	very slightly soluble	fairly soluble.
(v) Combustibility etc.…	Combustible, burns with a blue flame ; non-supporter of combustion.	Non combustible ; ordinarily not supporter of combustion ; but supports combustion of ignited Mg.
(vi) Character of the oxide…	neutral to litmus solution.	Acidic, turns blue litmus soln wine-red
(vii) Action on lime water…	No action on lime water.	Lime water turns milky.
(viii) Action on caustic soda solution…	Forms sodium formate on heating under pressure.	Forms carbonate and finally bicarbonate.
(ix) Reducing property…	Reducing agent ; reduces CuO, Fe_2O_3 etc. at high temperature into Cu, Fe, etc.	Inself reduced to CO by C, Fe, Zn etc at red heat.
(x) Additive reaction…	Being unsaturated, it forms addition product with Cl_2, ie. $COCl_2$.	It does not form addition product.
(xi) Absorbent	Absorbed by caustic alkalis	Absorbed by ammoniacal Cu_2Cl_2 solution.

DESTRUCTIVE DISTILLATION OF COAL : COAL GAS

Mineral coal consists mainly of elemental carbon with which are mixed various organic compounds. Coal may be used directly as a fuel, or for the generation of more valuable types of fuel, such as (a) coal gas and coke by dry distillation, (b) gaseous fuels such as producer gas, etc., and (c) liquid fuels by hydrogenation.

25.12 Carbonisation of coal :—The destructive distillation of coal is known as carbonisation of coal. When coal is heated out of contact with air in a closed retort (dry distillation), it decomposes into several volatile and non-volatile products. On distillation, solid residue, *coke* is left in the retort and volatile smoky matter come out through an exit tube, which on cooling separate into two parts, —the condensed liquid and a gas. This gaseous product is called *coal-gas* and is collected in a tank to be used as a fuel. The liquid condensate separate into two layers : (i) heavy layer of *coal tar* and (ii) aqueous layer called *ammoniacal liquor.*

25 13 Manufacture of coal gas :—Bituminous coal is generally employed for the manufacture of coal gas as it gives rise to larger amount of gaseous and volatile matter than other varieties of coal. The quantity of gaseous product obtained depends on the temperature at which the coal is ditilled. High temperature carbonisation of coal (1000° – 1200°C) yields a larger volume of gas of low calorific value, where as low temperature carbonisation (600 – 800°C) gives much less gas of high calorific value and a crude light oil from which liquid fuels or motor spirits can be extracted. Low temperature coke is soft and is used for domestic purposes, while the high temperature coke is hard and is suitable for metallurgical purposes.

The diagram of a modern plant for manufacture of coal gas using vertical retorts shown in Fig 25.10. Powdered bituminous coal is distilled in a row of horizontal or vertical fireclay retorts. These are packed with pieces of coal almost upto the neck and are heated externally by the combustion of producer gas—the temperature is maintained at 700°C – 1000°C. The producer gas is prepared in producers built just below the retorts.

The volatile smoky products are led out by vertical iron *ascension pipes* and enter a horizontal iron trough known as the *hydraulic main* containing water at a fixed level. This serves as a water seal preventing the backflow of the gas when the retort-doors are opened for recharging. In the hydraulic main the temperature of the gas is lowered to about 60° – 80°C and condensation starts. Much of the tar and some ammonia contained in the gases separate and are collected in the hydraulic main. The gas leaving the main still contains some tar vapour along with gases like H_2S, NH_3, HCN, CS_2 etc. as impurities. The gas next passes through a series of air or water-cooled iron pipes, called *condensers*, where it is cooled to atmospheric temperature ; more tar and ammoniacal liquor separate which run into the tar well where tar plus ammoniacal liquor from the hydraulic main are collected. The liquid in the tar well separates out into two layers—the upper layer is mainly a a solution of ammonia and ammonium salts in water and is called *ammoniacal liquor* ; the lower layer is *coal tar*. The gas then passes through a rotary air-pump, called the *exhauster* (not shown in the figure), which drives the gas forward through the rest of the plant. It then passes first through a *scrubber-washer*, an iron tower packed with coke, where it is washed by a counter current flow of water to remove all traces of tar and ammonia. The scrubbed gas still

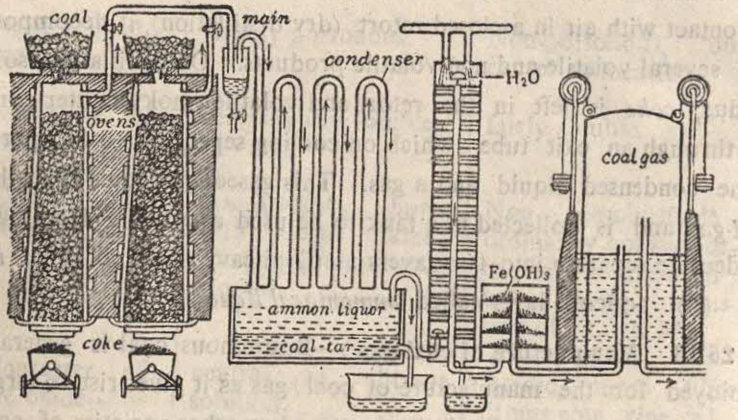


Fig. 25·10. Manufacture of Coal gas.

contains impurities like hydrogen sulphide, carbondisulphide and HCN, which are removed by passing the gas through *purifiers*, which are actually iron boxes containing hydrated ferric oxide spread on shelves. Hydrogen sulphide present in the gas is absorbed by moist ferric oxide to form ferric sulphide and is thus practically removed : $2Fe(OH)_3+3H_2S=Fe_2S_3+6H_2O$. The iron oxide, thus used up, is regenerated by exposure to air, whereby sulphur is separated : $2Fe_2S_3+3O_2+6H_2O=4Fe(OH)_3+6S$. When the iron oxide, after repeated uses, contains over 50% free sulphur, it becomes unsuitable as a 'purifier' and is then sold to the manufactures of H_2SO_4 as *spent oxide of iron* for the production of SO_2. The hydrocyanic acid, HCN, which is partly removed along with ammonia in the form of ammonium thiocyanate is now eliminated completely in the purifiers by reaction with ferric oxide, leading ultimately to the formation of ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$. Occasionally slaked lime is used in the purifiers instead of moist iron oxide, which absorbs H_2S. Carbondisulphide is also simultaneously removed :

$Ca(OH)_2+2H_2S=Ca(SH)_2+2H_2O$; $Ca(SH)_2+CS_2=CaCS_3+H_2S$.

The hydrogen sulphide liberated is absorbed in a second lime purifier. When iron oxide is used, carbondisulphide is usually left in the gas. In that case, it may be removed by passing the gas over heated nickel at 450°C, when it is converted into hydrogen sulphide by reacting with hydrogen already present, which is then removed as usual by moist ferric oxide :

$$CS_2+2H_2=2H_2S+C.$$

Finally the purified coal gas is stored in large gas-holders and is kept ready for use. After the carbonisation is over, the coke is pushed out of retorts by rams and quenched with water.

An approximate yield of main products from the carbonisation of 1 ton of coal is as follows :

Coal gas 13,000 cubic feet ; coal tar 120 lbs ; ammonium sulphate 25 lbs. ; coke 1500 lbs.

Composition of Coal gas :—The coal gas, obtained by the carbonisation of coal, is a mixture of several gases the composition of which varies with the type of the coal used and the temperature at which it is carbonised. A fairly representative sample has the following composition in percentage by volume :—

Nature of the constituents	Name of Gases	Percent by volume
(i) Non-illuminating, but heat producing ···	hydrogen ··· methane ··· carbonmonoxide ···	45 – 50% 30 – 45% 5 – 10%
(ii) Illuminants (unsaturated hydrocarbons)	ethy lene, acetylene, benzene and naphthalene ···	2·5 – 5%
(iii) Diluents (inert)···	nitrogen, oxygen and carbondioxide···	~10%
(iv) Impurities ···	hydrogen sulphide, hydrogen cyanide···	traces if any

Coal gas is colourless with a peculiar smell and possesses reducing properties. It burns with a smoky flame forming CO_2 and H_2O It should be handled with care as it contains carbon monoxide It is largely used in gas-burners in laboratories. It is an important gaseous fuel, which is employed both for domestic and industrial purposes. Its calorific value is approximately 700 BTU per. c. ft. Its earlier use for street-lighting has, however, been replaced by electricity. It also finds use in metallurgy.

25·14. By-products of Coal-gas industry :—The products obtained form coal-gas preparation are all very valuable and important. They are :—(1) coal tar, (2) ammoniacal liquor, (3) coke, (4) gas carbon, (5) spent oxide of iron.

(1) *Coal tar* : The thick heavy viscous dark liquid gives a large number of organic compounds on fractional distillation, such as benzene, toluene, naphthalene, authracene. carbolic acid, creosote

oil etc. These form the source materials for more than hundred marketable products. Many explosives, drugs, dyestuffs, perfumes, insecticides etc. are produced from these. The residue left after distillation of coal tar is pitch, which is used in road-making. Coal-tar itself is also used as a preservative of wood and a water proofing material for gunny bags, paper wrappers etc.

(2) *Ammoniacal liquor* : This liquid contains ammonia and ammonium salts. It is boiled with excess lime and the evolved ammonia is fixed by sulphuric acid as ammonium sulphate for its use as a fertiliser or led into water to get liquor ammonia of commerce.

(3) *Coke* : This is the residue left in the retort after the carbonisation of coal. It is extensively used as a solid fuel in industry and in domestic heating. It is also used as a reducing agent in metallurgy.

(4) *Gas carbon* : It is often deposited in the upper part of the retorts as a grey hard mass of carbon formed from the thermal decomposition of gaseous hydrocarbons in contact with the hot walls of retort. A good conductor of heat and electricity, it is used in making electrodes.

(5) *Spent iron oxide* : It is obtained in the purifiers and it contains free sulphur and cyanogen compounds. It is employed as a source of sulphur for sulphuric acid manufacture and as a source of potassium ferocyanide. *Gas lime* (also called *spent lime*) from the purifier is used as a mannure.

Coal-gas is not the only fuel used for domestic and industrial purposes. There are other kinds of fuel which are extensively used for heating. A brief account of different types of fuels is mentioned below.

25·15. *Fuels* : The term fuel is used to denote a substance which undergo combustion with oxygen of the air to liberate heat energy which are utilised for domestic and industrial operations. Fuels, which may be solid, liquid or gaseous, always contain, carbon and usually hydrogen.

(1) *Solid fuels* : Wood, wood-charcoal, coal, coke, peat, lignite

are common solid fuels. Of these, coal and especially coke are most widely used for domestic purposes and industrial plants. Wood occupies a secondary position in the total fuel balance, its use is gradually diminishing.

(2) *Liquid fuels* : Petroleum, which is stored underneath the surface of the earth in different areas, is the naturally occurring liquid fuel. On fractional distillation, it produces different liquid fuels, such as gasoline, kerosene, diesel oil etc—three products serve as excellent fuels for different purposes. Motor Cars, internal combustion engines, stoves, etc. are all dependent on these fuels.

(3) *Gaseous fuels* : For heating purposes, gaseons fuels are prefered, for they are the cleanest of fuels, which do not produce ash or tarry matter during combustion. The important gaseous fuels are natural gas, coal gas, producer gas, water gas, town gas, etc.

(i) *Natural gas* : It is mostly composed of methane along with other hydrocarbons. This gas comes out in large amount from the oil wells along with petroleum. It is a very cheap and convenient fuel having high heating value.

(ii) *Coal gas* : This is obtained during carbonisation of coal. The preparation and importance of coal gas has already been discussed earlier.

(iii) *Producer gas* : It is obtaned by forcing air through a bed of white-hot coke kept in a tall closed cylindical furnace (Fig 25.11) At the base, coke burns to carbondioxide, which is subsequently reduced to carbon monoxide by hot coke (1000°). The outcoming gas, called producer gas, contains approximately 30% CO and 65% nitrogen, some CO_2 is also present. The fuel is cheap, but because of the high percentage of non-coubustible nitrogen, the calorific value of the fuel is low.

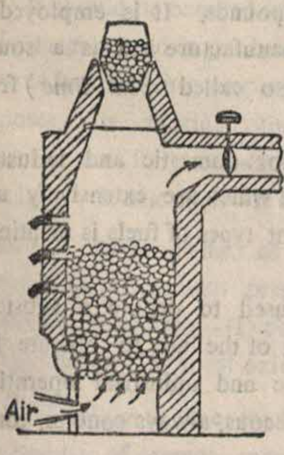


Fig. 25·11 Preparation of Producer gas

$$C + O_2 = CO_2 \; ; \; \Delta H = -97 \text{ Kcal.}$$
$$CO_2 + C = 2CO \; ; \; \Delta H = +39 \text{ Kcal.}$$

It is not stored and is straightway used as a fuel for heating coal gas retorts and in metallurgical furnaces.

(iv) *Water gas* : It is made by blowing steam through a bed of white-hot coke (1000°C). An endothermic reaction occurs, whereby a mixture of hydrogen and carbon monoxide are formed ($CO = 45\%$, $H_2 = 50\%$)

$$C + H_2O = CO + H_2 \; ; \quad \Delta H = +29 \text{ K cal.}$$

The temperature of the coke falls steadily as the reaction proceeds and some amount of carbondioxide is produced at low temperatures

$$C + 2H_2O = CO_2 + 2H_2 \; ; \quad \Delta H = +19 \text{ K cal.}$$

As the temperature falls, the supply of steam is cut off and air is blown in until the temperature is again raised to 1000°C. By an arrangement of values, the gases formed during the air blast (the blow, go to waste, and the gases formed during the steam-blast (the make) are led away to a gas-holder. In this way, steam and air are alternately blown through the hot coke and a supply of water-gas is maintained. Since both CO and H_2 are conbustible, the water-gas is a valuable fuel with a high heating power.

(v) *Semi-water gas* : It is made by passing moist air through a bed of hot coke. The amount of steam mixed with air is so regulated that cooling due to water gas reaction is balance by heat of formation of producer gas and the temperature is thus kept constant at 1000°C.

$$C + H_2O = CO + H_2 \; ; \; \Delta H = +29 \text{ K cal}$$

$$C + \tfrac{1}{2}O_2 + 2N_2 = CO + 2N_2 \; ; \quad \Delta H = -29 \text{ K cal.}$$

The product is called semi-water gas and has a composition of CO 30%, H_2 15%, N_2 50%, the remainder is chiefly CO_2. It is used as a fuel, and may be used as a source of nitrogen and hydrogen for the prepartion of ammonia by the Haber process.

(vi) *Town gas* : It is prepared from naphtha, available in appreciable quantities in petroleum refining. Liquid naphtha is vaporised and mixed with steam and then reformed at a high pressure of 30 atmospheres at a temperature of about 800°—900°C in presence of special nickel catalyst. This transforms the naphtha hydro carbon into CO and H_2 the change may be expressed as follows :

$$C_6H_{14}+6H_2O=6CO+13H_2$$

This gas stored in cylniders under pressure is very much used in domestic cooking as well as in small scale industries.

Now-a-days methods have been developed to convert powdered coal into liquid fuels (motor spirit, power alcohol) by causing it to combine with hydrogen, under high pressure and at elevated temperature. The coal is converted into a mixture of hydrocarbons, which on cooling yield a liquid (petrol).

Exercise – 25

1. (a) What is meant by allotropy ? Name the allotropes of two elements.
   (b) Name two compounds which exist in more than one form.
   (c) Compare the properties of diamond, graphite and charcoal. How would you show that all the allotropes of carbon are one and the same element ?
   (d) Ozone and oxygen are allotropes, but hydrogen and deuterium are not regarded as allotropes. Why ?
   (e) What is "activated charcoal ? How is it prepared ? Mention its uses.

2. What is the difference in arrangement of carbon atoms in diamond and graphite ? How does this arrangement influence their phyisical properties ?

3, How is carbon monoxide prepared in the laboratory ? Mention, giving necessary conditions, its reactions with (i) NaOH, (ii) H_2, (iii) CuO, (iv) chlorine and (v) nickel.

Why does carbon monoxide act as a poison ? How would you detect traces of carbon monoxide in foul air ?

4. Give two methods for preparing carbon dioxide in the laboratary. Indicate the reactions of carbon dioxide, stating necessary conditions with : (i) lime water, (ii) charcoal and (iii) caustic soda solution. Compare the properties of carbon dioxide with those of carbon monoxide.

5. How would you prove that carbon dioxide contains its own volume of oxygen ? Establish its formula.

6. (a) How would you identify two constituents in the following mixtures :
(i) CO_2 and CO , (ii) H_2 and CO , (iii) N_2 and CO_2?
(b) Why the amount of CO_2 in the atmosphere remains constant ?
(c) CO_2 is the product of combustion of carbon, yet magnesium burrs in it. How is this possible ?
(d) How would you show that calcium carbonate contains carbon ?
(e) Indicate the oxidation states of carbon in CO_2, CO and CH_4.
(f) Why coal-tar is considered more precious than coke ?
(g) How would you prove both CO_2 and CO are carbon compound ?
(h) How would you convert CO into CO_2 and vice versa ?
(i) Why H_2SO_4 is not used in the preparation of CO_2 from lime store ?

7. What is coal gas ? Indicate its approximate composition. How is the gas prepared, purified and stored ? What are the important by-products of coal-gas manufacture ? Mention the uses of each of the products.

8. Write short notes on :—

(i) Dry ice , (ii) Water gas , (iii) producer gas , (iv) artificial preparation of graphite , [v] amorphons carbon , [vi] photo synthesis , [vii] fire extinguisher, [viii] spent oxide of iron , [ix] town-gas and [x] ammoniacal liquor.

9. State what happens when—
(i) soiid sodium bicarbonate is heated, .
(ii) calcium carbonate is heated with coke,
(iii) carbondioxide is gradually passdd into lime water,
(iv) ignited magnesium inserted in a jar of carbondioxide,
(v) carbon monoxide is passed over finely divided nickel.

10. Describe the changes which take place when (a) air, and (b) steam, is passed over heated coke, and explain the bearing of the changes on the method used for the manufacture of water-gas. How is hydrogen obtained from water-gas ?

CHAPTER XXVI

BORON

Atomic number 5, Atomic weight 10·82, Density 2·34 gm/c.c., Electronic configuration $1s^2 2s^2 2p^1$, melting pt. 2300°C, boiling point 2500°C.

26·1. History and occurrence :—Borax, the most familiar compound of Boron was known from early times and was used as a flux· The element was, however, first isolated by Davy in 1807 by the electrolysis of moist Boric acid.

The element does not occur in the free state. In combination it occurs as (i) Boric acid, H_3BO_3 found in volcanic steam and in the hot springs and as (ii) Borates of which the following minerals are inportant—(a) Tincal or native borax, $Na_2B_4O_7$, $10H_2O$, (b) Colemanite, $Ca_2B_6O_{11}$, $5H_2O$, (c) Boronatro calcite, $Na_2B_4O_7$, $Ca_2B_6O_{11}$, $16H_2O$, and (d) Boracite, $MgCl_2$, $2Mg_3B_6O_{15}$. The main deposits are found in california (U.S.A.) and chile (S. America).

26.2. Preparation :—The element boron exists in two allotropic modifications : (i) amorphous and (ii) crystalline.

(i) Amorphous boron is prepared :

(a) by heating boron trioxide with sodium, potassium, magnesium or aluminium in a covered crucible.

$$B_2O_3+3Mg=3MgO+2B$$
$$B_2O_3+6K=3K_2O+2B$$

(b) by heating potassium borofluoride with potassium or magnesium in a covered curcible.

$$KBF_4+3K=4KF+B.$$

After the reaction is over, the fused mass is then cooled. The product is boiled with dilute hydrochloric acid to remove any metal or metallic borides. The product is then wnshed with hot water and finally dried in a steam oven, when the brown coloured amorphous boron is obtained.

(ii) Pure crystalline boron is obtained as a black, hard solid by fusion of amorphous boron followed by crystallisation or reduction of boron trichloride or tribromide vapour with hydrogen in an electric arc or in contact with electrically heated filament of tungsten or tantalum at about 1200°C.

$$2BCl_3+3H_2=2B+3HCl.$$

The so-called crystalline boron (adamantive boron) obtained by fusing amorphous boron with aluminium and then crystallising boron from molten aluminium, is nothing but aluminium boride with variable composition.

26·3. Properties :—Crystalline boron is very hard, almost as hard as diamond, and characterised by a matallic lustre with poor electrical conductivity. It is chemically inert and may be strongly heated in air without being attacked. It is hardly attacked by hot concentrated nitric and sulphuric acid and not at all by boiling concentrated hydrochloric or hydrofluoric acid. However, it is vigorously attacked by fused sodium peroxide.

On the other hand, amorphous boron is much more reactive. (i) When heated in air to 700°C, boron forms boron trioxide, B_2O_3 and also boron nitride, BN. Boron nitride is decomposed by steam :

$$BN+3H_2O=NH_3+H_3BO_3.$$

(ii) Boron enters into combination with the halogens and sulphur when heated. With chlorine, it forms boron trichloride, which is hydrolysed by water, yielding boric acid :

$$2B+3Cl_2=2BCl_3 : \ BCl_3+3H_2O=3HCl+H_3BO_3.$$

Boron trifluoride is obtained by the spontaneous combustion of boron in fluorine. It is also decomposed by water yielding boric acid and fluoboric acid :

$$4BF_3+3H_2O=H_3BO_3+3HBF_4.$$

Boron also combines with carbon when heated in an electric furnace giving boron carbide, B_4C, which is the heardest substance known. This is made technically by heating B_2O_3 and coke in an electric furnace :

$$2B_2O_3+7C=B_4C+6CO.$$

(iii) Water is without action on boron, but concentrated sulphuric acid and nitric acid oxidise it to boric acid :

$$B+3HNO_3=H_3BO_3+3NO_2$$
$$2B+3H_2SO_4=2H_3BO_3+3SO_2$$

But it is not attacked by hydrochloric acid.

(iv) Just like silicon, boron reacts with fused alkalies to form borates and hydrogen :

$$2B+2KOH+2H_2O=2NaBO_2+3H_2.$$

(v) Boron combines with many metals at high temperatures in the electric furnace forming metallic borides, which are very hard substances :

$$3Mg+2B=Mg_3B_2$$

(vi) Boron hydrides :—When magnesium boride, Mg_3B_2 is treated with hydrochloric acid in the absence of air, a mixture of volatile boron hydrides is obtained. Several pure compounds may be isolated by fractional distillation of the liquid obtained by cooling the hydride mixture with liquid air. The two simplest boron hydrides are borobutane, B_4H_{10} and boroethane, B_2H_6. They are highly reactive and readily hydrolysed by water yielding hydrogen and boric acid.

$$B_2H_6+6H_2O=2H_3BO_3+6H_2$$

In its chemical properties boron resemble silicon to a great extent.

26·4. Oxide—Boron trioxide, B_2O_3 is a colourless glassy solid. It is prepared when boron is burnt in oxygen : $4B+3O_2=2B_2O_3$. It is generally prepared by heating boric acid to redness :

$$2H_3BO_3=B_2O_3+3H_2O.$$

It is an acidic oxide giving rise to boric acid, when dissolved in water. Hence it is called boric anhydride.

$$B_2O_3+3H_2O=2H_3BO_3.$$

Boron trioxide also shows weakly basic properties, e.g. it gives phosphate, BPO_4 with phosphoric acid, and boron hydrogen sulphate, $B(HSO_4)_3$ with sulphur trioxide.

$$B_2O_3+2H_3PO_4=2BPO_4+3H_2O$$

X-ray analysis, however, has established that these compounds are not salts.

26·5. Boric Acid, H_3BO_3 :—In the solid state boric acid exists in three different forms : Orthoboric acid, H_3BO_3 ; metaboric acid. HBO_2 ; and pyroboric acid, $H_2B_4O_7$. But in aqueous solution meta and pyro-boric acids are changed into orthoboric acid.

Orthoboric acid H_3BO_3. also called boracic acid, is found in the saffioni, i.e., steam jets of the volcanic vapours in Tuscany—this on condensation and subsequent concentration produces boric acid.

Preparation :—(i) Orthoboric acid is generally prepared by adding excess of hydrochloric acid to a hot concentrated solution of borax. The liquid on cooling gives soft, silky crystals of boric acid. These are washed with cold water and recrystallised from hot water.

$$Na_2B_4O_7+2HCl+5H_2O=2NaCl+4H_3BO_3.$$

(ii) On a commercial scale boric acid is mainly prepared from colemanite, $Ca_2B_6O_{11}, 5H_2O$. The powdered mineral is suspended in hot water and sulphur dioxide is streamed into this suspension when calcium sulphite and boric acid are formed. $CaSO_3$ dissolves in excess of SO_2 to form calcium bisulphite and crystals of boric acid separate out from the solution on cooling.

$$Ca_2B_6O_{11}+2SO_2+9H_2O=2CaSO_3+6H_3BO_3$$
$$2CaSO_3+2H_2O+2SO_2=2Ca(HSO_3)_2.$$

Properties :—(t) Ordinary boric acid or orthoboric acid crystallises in soft, silky, pearly white flakes having a greasy touch. It is slightly soluble in cold water, more so in hot water. It is volatile in steam and it gives a green colouration to a non-luminous flame.

(ii) Orthoboric acid loses water on gradual heating and produces different boric acids and ultimately a glassy mass of boron trioxide. The change can be shown as follows :

$$\underset{\text{ortho}}{H_3BO_3} \xrightarrow{100°C} \underset{\text{meta}}{HBO_2} \xrightarrow{140°C} \underset{\text{pyro}}{H_2B_4O_7} \xrightarrow{\text{Red heat}} \underset{\text{oxide}}{B_2O_3}$$

$$H_3BO_3-H_2O=HBO_2 \text{ (meta boric acid)}$$
$$4HBO_2-H_2O=H_2B_4O_7 \text{ (pyro boric acid)}$$
$$H_2B_4O_7-H_2O=2B_2O_3 \text{ (Boron trioxide)}$$

(iii) Orthoboric acid is a very weak acid (weaker than carbonic acid). It turns blue litmus wine-red and moist turmeric paper brown but has no actipn upon methyl orange. It is not posslble to titrate the acid accurately against standard alkalis. However, in the presence of glycerol or mannitol it can be titrated against sodium hydroxide solution using phenolphthalein as indicator. It then acts as a comparatively strong monobasic acid :

$$H_3BO_3 + NaOH = NaBO_2 + 2H_2O.$$

Uses :—(1) It is used in medicine, as a mild disinfectant, as borated cotton, boracic powder and ointment. (2) It is also used in the manufacture of enamels and glazes for pottery, and (3) in the preservation of milk.

26·6. Borates :—Salts from the three boric acids are known as, ortho—, meta—and pyroborates. The orthoborates are unstable, but the metaborates and pyroborates are stable compounds. Sodium pyroborate, $Na_2B_4O_7$ or borax is the most important of all borates.

26·7. Borax, $Na_2B_4O_7$, $10H_2O$:—This is the most familiar compound of boron. It is prepared from :

(i) Colemanite by digestion with hot sodium carbonate solution. Finely powdered colemanite is boiled with sodium carbonate solution, when $CaCO_3$ precipitates out and a mixture of borax and sodium metaborate is formed.

$$Ca_2B_6O_{11} + 2Na_2CO_3 = 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2.$$

The clear solution from the top is taken off and is then allowed to crystallise, when large colourless crystals of borax separate out. The sodium metaborate in the mother liquor is then converted into borax by passing in carbondioxide through the solution the second crop of crystals of borax separates out on crystallisation, leaving the sodium carbonate in solution.

$$4NaBO_2 + CO_2 = Na_2B_4O_7 + Na_2CO_3.$$

(ii) Boric acid by digesting a hot solution of boric acid with the proper amount of soda ash. The solution on cooling yields crystals of borax.

$$4H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + 6H_2O + CO_2$$

(iii) Tincal, the native borax, by treating natural tincal with hot water and subsequently evaporating the clear solution, when crystals of borax separate out.

Properties : (i) Ordinary Borax, $Na_2B_4O_7$, $10H_2O$, is a white efflorescent solid soluble in water. It separates as monoclinic crystals below 62°C ; but above this octatedral borax, $Na_2B_4O_7, 5H_2O$ separates. (ii) The aqueous solution of borax is alkatine due to hydrolysis :

$$Na_2B_4O_7+7H_2O \rightleftharpoons 2NaOH+4H_3BO_3.$$

Boric acid is so weak that a solution of borax (like sodium carbonate) may be titrated against a mineral acid using methy orange as indicator.

$$Na_2B_4O_7+2HCl+5H_2O=2NaCl+4H_3BO_3.$$

Borax solution gives a pink colour with phenolphthalein : the colour however is dischanged on the addition of glycerine which prevents the hydrolysis of borax.

(iii) On being heated, borax parts with water, swells up due to liberation of steam and fuses to a colourless transparent glassy bead consisting of sodium metaborate and boron trioxide.

$$Na_2B_4O_7, 10H_2O=Na_2B_4O_7+10H_2O$$
$$Na_2B_4O_7=2NaBO_2+B_2O_3$$

The so-called 'borax bead' can dissolve a number of metallic oxides to form metaborates which in certain cases posses characetristic colours. Thus when a copper salt is used on the bead and heated in oxidising flame, a blue bead is obtained (Green when hot) due to cupric metaborate : $CuO+B_2O_3=Cu(BO_2)_2$ This on heating in a reducing flame turns red due to the formation of metallic copper. The borax bead test, used in qualitative analysis to detect the basic radical in a compound, is based on this fact. The above table shows the colour of the borax bead with different compounds.

Compounds of	Colour of borax bead	
	oxidising flame	reducing flame
Copper	Green (hot), blue (cold)	red (opaque)
Cobalt	Deep blue	Deep blue
Chromium	Green	Green
Iron	Yellow	Bottle Green
Manganese	Amethyst (pink)	Colourless
Nickel	Reddish brown	Grey (opaque)

Uses :—(i) Borax is used in the manufacture of optical and hard glass, enamels and glazes for pottery. Jena and pyrex glasses contain boric oxide. (ii) it is used as an antiseptic in making medicinal soaps, in the preservation of food, as a flux in soldering, for stiffening candle wick, for glazing paper, playing cards, linen etc. and in laundry work. (iii) It is used in borax bead test in qualitative analysis.

Test for boric acid and borates :—

(1) Cobalt nitrate test—When a borate moistened with cobalt nitrate solution is heated on charcal in an oxidising flame, a blue mass is obtained.

(2) Ethyl-borate test.—To a paste of concentrated H_2SO_4 and a borate, ethyl alcohol is added and heated. The vapour coming out contains ethyl borate which on ignition burns with a green-edged flame.

Excercise—26

1, (a) What is borax ? How is its obtained on a large scale ? Explain the uses of borax in qualitative analysis.

(b) How may (i) boron, (ii) boron trichloride be obtained from borax ?

(c) Why does a solution of borax react alkaline.

2. Describe how you would prepere boric acid from borax. What experiments would you make in order to show that boric acid is a weak acid ? How are borates recognised qualitatively ?

3. Write notes on :—

(a) Borax-bead test

(b) action of heat on orthoboric acid

(c) allotropic modifications of boron.

CHAPTER XXVII

SILICON

Atomic number 14, Atomic weight 28·06, m. p. 1420°C, Density 2·49 (crystalline), 2·35 (amorphous), Electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^2$.

The element silicon is next to carbon in the fourth group of the periodic table. There is a diagonal relationship between silicon and boron which is an element of the third group of the periodic table, as such the silicon chemistry resembles that of boron in many respects.

27·1. Occurrence : Silicon is not known to occur free in nature ; but next to oxygen, it is the most abundant element comprising about 25% of the mass of the earth's crust. It occurs always combined with oxygen and usually with other elements as well. It occurs as silicon dioxide or silica in various forms, such as quartz, agate, flint and sand. As silicates it occurs in clay, in many rocks and in the soil.

27.2. Preparation :—Silicon exists in two allotropic modifications. One, *amorphous silicon*, is a light brown powder, the other, *crystalline silicon*, is a hard crystalline solid.

Amorphous silicon is prepared :

(i) by heating strongly an intimate mixture of dry silica (quartz or sand) and magnesium powder in a porcelain crucible : $SiO_2 + 2Mg = Si + 2MgO$. Magnesium oxide and unreacted silica are removed from the resulting mass by washing successively with hydrochloric and hydrofluoric acids.

(ii) by heating sodium or potassium in a current of silicon tetrachloride vapour : $SiCl_4 + 4K = Si + 4KCl$.

Crystalline silicon is prepared :

(i) by reducing silica with coke in an electric furnace :

$$SiO_2 + 2C = Si + 2CO.$$

(ii) When silicon is crystallised from solution in molten zinc or aluminium, and consequently when silicon is prepared by the reduction of its compounds with these metals :

$$3SiCl_4 + 4Al = 4AlCl_3 + 3Si$$

$$3SiO_2 + 4Al = 2Al_2O_3 + 3Si.$$

27·3. Properties :—Amorphous silicon is a light brown powder with a sp. gravity of 2·35. When heated strongly in air, it burns vigorously to form the dioxide, SiO_2. Amorphous silicon unites spontaneously with fluorine forming silicon tetrafluoride, SiF_4, and when heated, with chlorine, bromine and iodine yielding corresponding halides. These halides are decomposed by water : $SiCl_4 + 4H_2O = 4HCl + Si(OH)_4$ (orthosilicic acid). It is dissolved neither in water nor by any single acid, but it is attacked by a mixture of nitric and hydrofluoric acids. It dissolves in a concentrated solution of an alkaline hydroxide or in fused sodium carbanate : $Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2$; $Si + Na_2CO_3 = Na_2SiO_3 + C$. At the temperature of electric furnace, silicon melts and combines directly with magnesium, carbon and some other elements to form silicides, e.g., Mg_2Si, SiC etc.

Crystalline silicon forms yellow to brown octahedral crystals with metallic lustre. crystalline silicon is not attacked by oxygen, even at high temperatures ; in other respects its chemical properties resemble those of amorphous silicon, though it is less reactive than the amorphous variety.

27·4. Uses :—Silicon is used in the preparation of alloys such as silicon-brouze, ferro-silicon and acid resisting silicon steel. It is used as a de-oxidiser in making steel. Silicon chips are used in semi-conductor devices such as transistors.

27.5. Silica or silicon dioxide, SiO_2 :—Silicon has only one oxide, namely silicon dioxide or silica, SiO_2. Silica occurs in nature in vast quantities and the question of its preparation does not arise.

Silica occurs in nature both in crystalline and amorphous forms. Ordinarily crystalline silica occurs in nature as α-quartz. Sand is also really quartz crushed by forces of nature, specially by water and only outwardly appears to be amorphous. Pure silica or quartz is colourless or white but it is sometimes brown or grey due to admixture with iron oxide and other impurities.

Sometimes colourless transparent beautiful crystals of quartz are obtained, these are called *rock-crystals*. These are almost as hard as diamond. Traces of dissolved metallic oxides often give rise to excellent colours to transparent quartz crystals. They are then considered as precious stones. *Amethyst* is quartz containing a little dissolved manganese oxide, *cat's eye* contains a little asbestos dissolved in quartz. These stones are often cut into suitable dazzling shapes and are valued as gems.

Of the amorphous varieties of silica, the most well-known are *opal*, *agate* and *fiint*. The white earth-like matter, *kieselguhr*, derived from thc bodies of "diatoms" is also mainly amorphous silica. Silica also occurs in some plant cells like those of bamboo and also in sponges.

Pure Silica ; It is prepared by fusing calcium silicate with sodium carbonate. The fused mass is extracted with boiling water when sodium silicate dissolves. It is separated by filtration and the filtrate, on being boiled with conc. HCl, gives a deposit of pure white coloured slica.

$$CaSiO_3 + Na_2CO_3 = CaCO_3 + Na_2SiO_3$$
$$Na_2SiO_3 + 2HCl = 2NaCl + H_2O + SiO_2$$

Properties of Silica ; (i) Crystalline α-quartz undergoes change in its crystalline from when gradually heated. Inf act, it can exist in four different crystalline forms until it melts at 1710°. These are

$$\alpha\text{-quartx} \overset{573^\circ}{\rightleftharpoons} \beta\text{-quartz} \overset{870^\circ}{\rightleftharpoons} \beta\text{-tridymite} \overset{1470^\circ}{\rightleftharpoons} \beta\text{-cristobalite} \overset{1710^\circ}{\rightleftharpoons} \text{liquid}$$

(ii) When sand or quartz is heated in oxyhydrogen flame, it melts at 1710°C into a transparent viscous colourless liquid looking like glass. It is also malleable like glass and can be given any desirable shape. It is known as *silica-glass*, density 2.2 gm/c.c. It has some special qualities. It can stand high temperature and would soften at about 1500°C. Its co-cfficient of expansion is very low. It is transparent to ultraviolet light. It is *inert* towards acids. *Vitreosil* is an opaque variety of silica-glass.

(iii) Silica is an acidic oxide, but it is insoluble in water. When heated with alkalis, it forms silicate salts.

$$2KOH + SiO_2 = K_2SiO_3 + H_2O$$
$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

(iv) Silica is not attacked by any acid except HF. It forms silicon tetraflouride on reaction with HF.

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

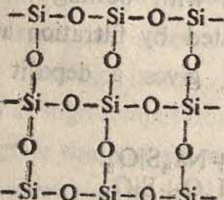
(v) Silica, when heated with excess carbon, in an electric furnace produces silicon carbide or *carborundum.*

$$SiO_2 + 3C = SiC + 2CO$$

(vi) A mixture of silica and coke when strongly heated in a current of chlorine yields silicon tetrachloride.

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$$

Silica is a *giant molecule*, like a diamond crystal ; in which each silicon atom is linked to four oxygen atoms tetrahedrally, each oxygen being shared with another tetrahedron. It differs markedly in this respect from carbondioxide which is a gas at room temperature and forms discrete molecules.



Uses of silica :—*Sand* is used is making glass, glaze, porcelain, mortar, silica-bricks etc. and as building materials. *Sand stone* Is used in making mill-stones. *Agate* finds use in making mortars and knife edges of balances. Colourless *quartz* is used for spectacle lenses aud for lenses and prisms in optical instruments. Coloured varieties of *quartz*, such as *amethyst*, *cat's eye* and *opal* are used as gems.

27·6. Silicic acid and silicates :—(i) meta-silicic acid, H_2SiO_3 is obtained in colloidal solution if a soluble silicate is treated with a dilute acid :

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3.$$

If the electrolytes are removed by dialysis a pure silicic acid sol may be prepared. Silicic acid is very weak acid. The colloidal solution readily sets to a gel which after drying is *silica gel*. It is an excellent detrydrating agent.

(ii) Ortho-silicic acid, H_4SiO_4 is made by the hydrolysis of silicon tetrahalide : $SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl$.

Sodium silicate, Na_2SiO_3, is prepared by fusing sand with nearly double its weight of sodium carbonate : $SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2$. It is soluble in water, and the solution is alkaline due to hydrolysis. Thick solution of sodium silieate, known as *water glass*, is used as an adhesive cement for joining pieces of china, as an adulterant of soap, and as a preservative for eggs. Many important silicates occur in rock minerals, examples are : Talc, Asbestos, Felspar, Kaolin, Mica etc. Most of them have very complex composition.

27·7. Glass :—A glass is the apparently solid substance which is produced when a mixture of silicates are melted and then the molten mass is supercooled to such an extent that it becomes apparently a transparent solid without undergoing crystallisation. As the liquid cools it becomes increasingly viscous, until it acquires the strength and rigidity of a crystalline solid. A glass is isotropic, it has no sharp melting point, but gradually softens and finally liquefies when heated.

All glass used for general purposes contains silica. Common glass has roughly the composition Na_2O, CaO, $6SiO_2$. In special glasses Na_2O may be wholly or partly replaced by K_2O, CaO by PbO, BaO or ZnO, SiO_2 by Al_2O_3, B_2O_3 or P_2O_5. A glass is made by fusing together sand and the necessary metallic oxides or carbonates.

Coloured glass is made by adding various metallic oxides or other substances to the molten glass is course of its preparation.

Glass is more or less resistant to the attack by all chemical reagents except *hydrofluoric acid*—alkalis, however, have very slow corroding action upon glass.

Exercise—27

1. Write what you know of the allotropes of silicon. How is silica obtained from it ? Describe the occurence, propertics and uses of silica.

2. Standing with sand how would you prepare (i) water glass, (ii) silicon tetrachloride and (iii) silica gel.

3. Why silicon dioxide is hard but carbondioxide is a gas ? What is glass ?

CHAPTER XXVIII

PHOSPHORUS

Formula P_4, Atomic number 15, Atomic weight 30·98, Electromic configuration $1s^2 2s^2 2p^6 3s^2 3p^3$.

28·1. History and occurrence :—Phosphorus was discovered by the alchemist Brand in 1674, who obtained it as a blackish solid by distilling concentrated and fermented urine. It was called phosphorus as it was found to glow in the dark. Scheele was the first to develop large-scale preparation of phosphorus from bone-ash (1777).

Phosphorus never occurs in the free state in nature. It is usually present as phosphate in different minerals, especially as calcium phosphate. Some of the important minerals containing phosphorus are :

Phosphorite, $Ca_3(PO_4)_2$; Fluorapatite, $3Ca_3(PO_4)_2$, CaF_2 ; Chlorapatite, $3Ca_3(PO_4)_2$, $CaCl_2$; Vivianite, $Fe_3(PO_4)_2$, $8H_2O$; Aluminium phosphate, $AlPO_4$.

Phosphorus is an essential constituent of all living, vegetable and animal matters. In many plant and animal tissues it is present as phosphoproteins. The bones of animals contain about 58% calcium phosphate.

28·2. Preparation of phosphorus :—Phosphorus exists in several allotropic forms : the two most familiar allotropes are (a) *white* (or *yellow*) *phosphorus* and (b) *red phosphorus.*

The phosphate minerals and bone-ash are the two important sources from which white phosphorus is manufactured.

(a) From Bone-ash :—In the older process white phosphorus is prepared from the calcium phosphate present in the bones. Bones are first freed from fat and organic matter by treating with carbon tetrachloride (which removes fat) and by boiling with water under pressure. On destructive distillation of degreased bones, a black-mass, called *bone charcoal* is obtained which contains calcium phosphate and carbon. Heated strongly in air, carbon escapes as carbon dioxide leaving the residue called *bone-ash* which contains more than 80% $Ca_3(PO_4)_2$. This bone-ash is digested with hot 60% H_2SO_4 in big pans when calcium sulphate separates out and phosphoric acid remains in the liquid.

$$Ca_3(PO_4)_2+3H_2SO_4=3CaSO_4+2H_3PO_4.$$

Calcium sulphate is filtered off and the solution is concentrated by slow evaporation when syrupy phosphoric acid is obtained. This is the common method of preparation of phosphoric acid, soft phosphatic minerals can also be used instead of bone-ash for this purpose.

The syrupy phosphoric acid is then mixed with powdered coke and heated to dryness. The dried mass is then heated to reducss in fire clay retorts having necks dipping under water. The phosphoric acid is first converted into *meta-phosphoric acid* and the latter is reduced to elementary phosphorus by coke. A mixturc of hydrogen and carbon monoxide escape and phosphorus vapour condenses into its solid state under water.

$$H_3PO_4=HPO_3+H_2O\ ;\ 4HPO_3+12C=P_4+12CO+2H_2.$$

(b) **The modern electrothermal process** :—In the modern *Parker-Robinson* process, white phosphorus is produced by heating a phosphate mineral with sand and coke at a high temperature in an electric furnace

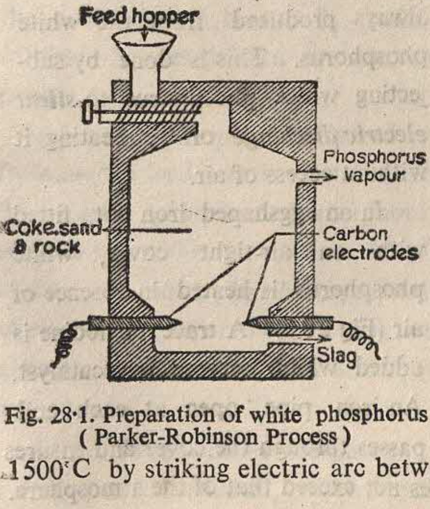


Fig. 28·1. Preparation of white phosphorus (Parker-Robinson Process)

A mixture of powdered phosphatic mineral (or bonesah), coke and sand is introduced through the hopper by a serew conveyer into a closed electric furnace made of brick work (Fig 28.1). The charge is heated to a high temperature of about 1200° – 1500°C by striking electric arc between two stout carbon electrodes fixed near the bottom of the furnace. At the high temperature of the arc, sand, the non-volatite anhydride of silicic acid, attacks the calcium phosphate and displaces the volatile phosphorus pentoxide :

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5.$$

The phosphorus pentoxide is then reduced by the coke to phosphorus : $2P_2O_5 + 10C = P_4 + 10CO$. Phosphorus vapour and carbon monoxide escape by an exit pipe at the top and are led into water. Phosphorus vapour condenses to yield solid ***white phosphorus*** and CO escapes into the air. The molten calcium silicate is run off at the bottom as a slag.

To obtain pure phosphorus, the crude phosphorus thus obtained is melted under hot water and separated from sand and clay particles. It is then treated with chromic acid solution (i.e. $K_2Cr_2O_7 + H_2SO_4$). Some of the impurities are oxidised, some dissolve and the rest separate as scum. The molten phosphorus is then filtered by passing through canvas or chamois leather. The purified white phosphorus is cast into sticks and preserved under water as it inflames at very low temperatures in contact with air.

28·3. Preparation of Red phosphorus :—The phosphorus from the phosphates by the methods described above is "white phosphorus"—sometimes called *yellow phosphorus*. Red phosphorus is always produced from the white phosphorus. This is done by subjecting white phosphorus to *silent electric discharge* or by heating it without access of air.

In an eggshaped iron pot, fitted with an air-tight cover, white phosphorus is heated in absence of air (Fig 28.2) A trace of iodine is added which serves as a catalyst. An iron pipe, open at each end, passes through the cover and ensures that the pressure inside the pot does not exceed that of the atmosphere.

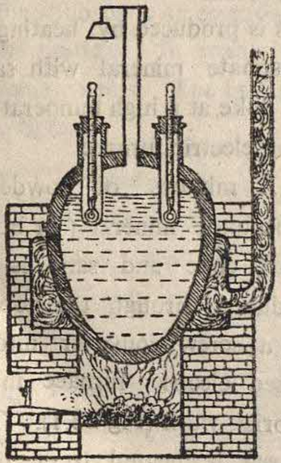


Fig. 28·2. preparation of red phosphorus

The temperature is kept at 240°C. A portion of phosphorus is oxidised by oxygen of air in the pot, and the rest is slowly transformed into solid red phosphorus. The product is cooled, ground under water and boiled with caustic soda solution to remove phosphoric acid and unchanged white phosphorus. The insoluble red phosphorus is filtered and washed with hot water. It is then dried in air.

Red phosphorus is not spontaneously inflammable in air, so it is not necessary to keep red phosphorus under water.

Conversion of red phosphorus to white phosphorus and vice versa :

(i) **Red to white**—If red phospoorus is heated above 550°C in an inert atmosphere and vaporised, the vapour condenses into solid white phosphorus.

(ii) **White to red**—When white phospharus is heated at 240°C in a closed vessel in absence of air (with a little iodine as a catalyst), it is transformed into red phosphorus.

28·4. Allotropy of phosphorus :—Phosphorus exhibits allotropy. As already stated, the most familiar allotropes of phosphorus are white and red phosphorus. White phosphorus formed by the condensation of phosphorus vapour is metastable at ordinary temperature and is slowly transformed into the stable red form with the evolution of heat : P_4 (white) $= P_4$ (red) ; $\Delta H = -4 \times 4400$ caloies. Besides the red phosphorus other stable forms of phosphorus are :

(a) *violet phosphorus* prepared by crystallising white phosphorus from molten lead. It is crystalline and non-conductor of electricity, (b) *scarlet phosphorus*, amorphous, prepared by boiling a dilute solution of white phosphorus in phosphorus tribromide for several hours, (c) *black phosphorus*, crystalline and fairly good conductor of electricity, prepared by heating white phosphorus at 200°C under a pressure of about 10,000 atmospheres. It resembles graphite in appearance.

28·5. Properties of phosphorus : White phosphorus :—(i) It is a soft, waxy, translucent, white or pale yellow crystalline solid which can be cut with a knife. It has a garlic smell. Its sp. gr. is 1·83 gm/cc. and m.pt. is 44°C. It is practically insoluble in water but readily soluble in carbon disulphide, ether, benzene, olive oil etc. It is a non-conductor of heat and electricity. It is highly poisonous —the lethal dose for a man is 0·15 gm. It sublimes at room temperature, giving off a poisonous vapour. The density of the vapour between 500° and 1000° indicates that the molecular formula of the vapour is P_4 ; the molcular formula of white phosphorus dissolved in benzene or in carbon disulphide is also found to be P_4.

(ii) White phosphorus is a very active element. It ignites in air at the low temperature of 35°C, yielding phosphorus pentoxide, and hence phosphorus is always kept and handled under water :

$$P_4 + 5O_2 = 2P_2O_5.$$

Exposed to air at the room temperature white phosphorus undergoes spontaneous oxidation, yielding white fumes of a lower oxide and some ozone and emitting a green light easily visible in the dark, known as the *glow of phosphorus.* This phenomenon is commonly known as *phosphorescence* ; but the emission of this faint light is accompanied by chemical reactions, it is better called *chemiluminescence.* The energy of oxidation is not liberated in the form of heat, but emitted as light.

Experiments :—(a) A solution of phosphorus in CS_2 is poured on a filter paper, the carbondisulphide rapidly evaporates, and the phosphorus inflames, giving white fumes of P_2O_5

(b) *Cold flame experiment* : A few pieces of dry white phosphorus are kept in a flask covered with glass wool. The air in the flask is driven out by a continuous current of CO_2-gas. The flask is then heated on a water-bath. The vapours of phosphorus comes out through a narrow exit tube. As soon as the vapour comes in contact with air, it begins to phosphoresce with a green flame. The flame is cold to the hand and will not ignite a match.

(c) Water containing a very small quantity of phosphorus is boiled, the steam is found luminous in the dark.

(iii) White phosphorus inflames spontaneously in halogens, yielding halides of phosphorus :

$$P_4 + 6Cl_2 = 4PCl_3 \ ; \ P_4 + 10Cl_2 = 4PCl_5 : P_4 + 6I_2 = 4PI_3.$$

It reacts violently with sulphur to produce phosphorus sulphides :

$$P_4 + 6S = 2P_2S_3 \ ; \ P_4 + 10S = 2P_2S_5.$$

Metals like sodium, potassium, calcium etc. react with phosphorus to give the corresponding phosphides, e.g., Na_3P, Ca_3P_2 etc.

(iv) When boiled with strong alkalis, white phosphorus gives phosphine gas and hypophosphite salt is formed :

$$P_4 + 3NaOH + 3H_2O = \underset{\text{(phosphine)}}{PH_3} + \underset{\text{(sodium hypophosphite)}}{3NaH_2PO_2}$$

(v) White phosphorus is oxidised to phosphoric acid when boiled with concentrated nitric acid :

$$P_4 + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2.$$

Experiment : Fire under water : A mixture of white phosphorus and potassium chlorate are kept in a jar under water. concentrated sulphuric acid is then added carefully from a dropping furnel to the solid mixture when phosphorus ignites under water giving bright flashes. This is "fire under water".

(vi) White phosphorus, when added to solutions of salts of of copper, silver or gold, reduces them first to phosphides and then finally to the metals.

$$3P_4 + 12CuSO_4 + 24H_2O = 4Cu_3P + 8H_3PO_3 + 12H_2SO_4$$
$$P_4 + 10CuSO_4 + 16H_2O = 10Cu + 4H_3PO_4 + 10H_2SO_4$$
$$2P_4 + 15AgNO_3 + 12H_2O = 5Ag_3P + 3H_3PO_4 + 15HNO_3.$$
$$P_4 + 20AgNO_3 + 16H_2O = 20Ag + 4H_3PO_4 + 20HNO_3.$$

N.B. White phosphorus must never be touched with fingers. If white phosphorus has been accidentally dropped on the hand, it may be removed by washing with cupric sulphate solution.

Red phosphorus : (i) It is a reddish violet crystaliine solid with a sp. gr. 2·20 gm/c.c. It has no definite m. pt. but softens at a temperature above 500°C. It is insoluble in water and in other organic solvents. It is not a poisonous substance. It is a feeble conductor of electricity.

(ii) Red phosphorus is chemically less reactive than the white variety. It is quite stable at the ordinary temperature. It does not phosphoresce in air, but when heated in air or oxygen above 260°C, it burns to phosphorus pentoxide. It burns in chlorine when heated, but it does not ignite spontaneously at room temperature.

(iii) It does not react with caustic soda to produce phosphine, but it dissolves rapidly in warm concentrated nitric acid. It does not exhibit reducing action, like white phosphorus, towards solutions of copper or silver salts.

28·6. Uses :—(a) White pyosphorus is used for making red phosphorus (which has an important commercial value), phosphorus pentoxide, hypophosphite salts, phosphorus halides, incendiary bombs and smoke-screen. Previously white phosphorus was used for making "lucifer matches" but this has been banned for its poisonous effect.

(b) Red phosphorus is mostly used in preparing safety matches. It is also required in the preparation of HBr and HI and also in the synthesis of some organic substances.

Comparison between white phosphorus and Red phosphorus : The physical and chemical properties of white and red phosphorus are summerised as follows :

Property	White phosphorus	Red phosphorus
(1) Colour and smell	White or pale yellow waxy solid with garlic smell	Red opaque solid with no smell
(2) Mlting ponit	44·1°C	No sharp m. pt. but it softens at 590°C.
(3) Ignition temp. in air	35°C	260°C
(4) Density	1·82 gm/c.c.	2·20 gm/c.c.
(5) Solubility	Insoluble in water but soluble in carbondisulphide	Insoluble in water, carbondisulphide.
(6) Chemical activity	Highly reactive	comparatively less reactive.
(7) Action of heat	changes to Red phosphorus at 240°C	changes to white phosphorus at 550°C.
(8) Reaction with		
(i) oxygen	oxidised to P_2O_5 at 35°C	oxidised to P_2O_5 at 260°C
(ii) halogen	readily forms halides at ordinary temperature	Halides are formed slowly, but quickly on heating
(iii) sulphur	Reacts violently	Reacts slowly
(iv) couc HNO^3	Reacts violently	Reacts slowly
(v) hot alkali solution	Dissolves evolving PH_3	No action
(9) physiological action	Poisonous	Non-poisonous
(10) phosphorescence	present	absent
(11) stability	metastable allotrope	stable allotrope

N. B. The vapour of phosphorus consists of molecules containing 4 atoms arranged tetrahedrally and are linked to one another by covalent bonds Liquid phosphorus has the same molecular structure, and probably crystalline white phosphorus also. There is considerable strain is tetrahedral P_4 molecules in white phosphorus, and hence its high reactivity. The black and red phosphorus crystals form giant molecules—energy is required to rupture the P – P bonds in these molecules before they can react, hence they are less reactive chemically.

COMPOUNDS OF PHOSPHORUS

The compounds of phosphorus are generally covalent and may be classified into two main groups—those in which the phosphorus atom shows a covalency of three and those in which it shows five.

28.7. **Hydrides of Phosphorus** :—Two well-defined hydrides are known : (i) phosphine or phosphorated hydrogen, PH_3 which is gaseous and (ii) Liquid phosphorus dihydride or hydrogen phosphide, P_2H_4. Of the two, phosphine is more important.

Phosphine :—*Preparation*—(i) phosphine is prepared in a very impure condition by boiling white phosphorus with strong sodium or potassium hydroxide solution. Pieces of white phosphorus and a 30 to 40 percent solution of caustic soda are taken in a flask fitted with an inlet tube dipping in the solution and a delivery tube. (Fig. 28·3). The free end of the delivery tube dipps under water in a trough. The air in the flask is displaced by a current of coalgas continuously bubbled through the solution (Since the mixture of air and impure phosphine is spontaneously explosive), the flask is then heated when phosphine gas is formed along with sodium hypophosphite :

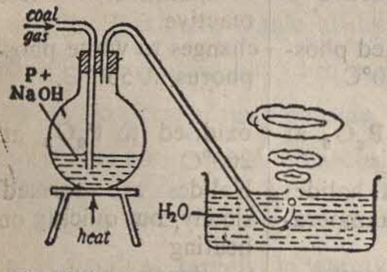


Fig. 28·3. ureparation of phosphine

$$P_4+3NaOH+3H_2O=PH_3+3NaH_2PO_2.$$

Impure phosphine thus formed escapes through the delivery tube, and as each bubble of the gas escapes into the air, it catches fire spontaneously and gives rise to a white vortex ring of phosphorus pentoxide. The rings go up in the air broadening in size. The spontaneous ignition of the gas thus prepared is due to the presence of P_2H_4, which catches fire in contact with air. Small amounts of hydrogen and P_2H_4 are always formed during the preparation of phosphine by this method due to the following reactions :

$$6P+4NaOH+4H_2O=P_2H_4+4NaH_2PO_2;$$
$$2P+2NaOH+2H_2O=H_2+2NaH_2PO_2;$$

Pure phosphine is not s pontaneouly inflammable in air. P_2H_4 may be removed by passing the impure gas through a U-tube kept in a freezing mixture, P_2H_4 condenses into liquid in the U-tube and the phosphine passes over. It is then collected over water which is no longer spontaneously inflammable. It contains traces of hydrogen. Non-spontaneously inflammable phosphine is obtained by using an alcoholic solution, instead of the aqueous solution of caustie soda.

(ii) Pure phosphine may be prepared by warming phosphonium iodide with caustic potash solution :

$$PH_4I + KOH = KI + PH_3 + H_2O.$$

The gas is washed with sodium hydroxide solution to remove hydriodic acid, dried with phosphorus pentoxide and collected over mercury.

(iii) Pure phosphine may also be prepared by the reaction of dil. H_2SO_4 upon aluminium phosphide, prepared by heating together aluminium powder and red phosphorus :

$$2AlP + 3H_2SO_4 = 2PH_3 + Al_2(SO_4)_3$$

Properties r—(i) It is a poisonous colourless gas with a smell of rotten fish. It is heavier than air and sparingly soluble in water—the solution is neutral to litmus.

(ii) It is not spontaneously inflammable but burus when lighted in air yielding phosphorus pentoxide :

$$2PH_3 + 4O_2 = P_2O_5 + 3H_2O.$$

It also burns in chlorine forming phosphorus trichloride :

$$PH_3 + 3Cl_2 = PCl_3 + 3HCl.$$

(iii) The gas is decomposed into red phosphorus and hydrogen when heated to 440°C, or sparking.

(iv) A mixture of phosphine and nitrous oxide explodes when sparked :

$$PH_3 + 4N_2O = H_3PO_4 + 4N_2.$$

(v) The dry gas is weakly basic and forms phosphonium salts (like ammonium salts) with halogen acids. The phosphonium salts are decomposed by alkali to phosphine (cf. ammonia).

$$PH_3+HI=PH_4I\ ;\ PH_4I+KOH=PH_3+KI+H_2O.$$

The phosphonium compounds undergo thermal dissociation into phosphine and the halogen acid :

$$PH_4Cl \rightleftharpoons PH_3+HCl$$

(vi) phosphine is a powerful reducing agent. It reduces copper sulphate solution into a black precipitate of cuprous phosphide Cu_3P. Silver nitrate is reduced to metallic silver when phosphine is passed into silver nitrate solution, a yellow intermediate addition compound being first formed :

$$PH_3+6AgNO_3=Ag_3P.\ 3AgNO_3+3HNO_3.$$
$$Ag_3P.\ 3AgNO_3+3H_2O=6Ag+3HNO_3+H_3PO_3.$$

Composition of phosphine :—A known volume of pure and dry phosphine gas is introduced in an eudiometer tube over mercury and the gas is completely decomposed by electric sparks. It is seen that 2 vols of phosphine on decomposition by sparking librate 3 volums of hydrogen, with the deposition of red phosphorus. Hence the formula of phosphine P_xH_3. The relative density of the gas being 17, its mol. weight is 34.

$\therefore$ $31x+3=34$ or, $x=1$, Hence the formula PH_3.

28·8. Comparison between phosphine and Ammonia :—These two compounds are the hydrides of two elements, phosphorus and nitrogen which belong to ths same group in the periodic table and there is a strong resemblance in the properties of these two important hydrides. Their properties can be compared as follows.

Ammonia	*Phosphine*
1. The molecular formula NH_3 a'covalent compound.	1. The molecular formula PH_3 a covalent compound.
2. A colourless gas with a pungent smell.	2. A colourless gas with a smell of rotten fish.
3. Highly soluble in water.	3. Sparingly soluble in water,
4. Decomposes into elements on strong heating.	4. Decomposes on heating into the elements.
5. It burns in excess Oxygen. $4NH_3+3O_2=2N_2+6H_2O$	5. It burns in air or Oxygen, $2PH_3+4O_2=P_2O_5+3H_2O$
6. It is basic, turns red litmus solution blue ; reacts with halogen acids to form ammonium salts. $NH_2+HI \rightarrow NH_4I$ Ammonium salts are decomposed by alkalis. $NH_4I+KOH=NH_3+H_2O+KI$	6. It has a basic character but does not turn red litmus solution blue ; reacts with halogen acids to form phosphonium salts. $PH_3+HI \rightarrow PH_4I$ Phosphonium salts are decomposed by alkalis. $PH_4I+KOH=PH_3+H_2O+KI$
7. Reacts spontaneously with chlorine. $NH_3+3Cl_2=NCl_3+3HCl$	7. Reacts spontaneously with chlorine. $PH_3+3Cl_2=PCl_3+3HCl$
8. Exhibits reducing property at higher temperature ; as $3CuO+2NH_3=3Cu+N_2+3H_2O$	8. Show strong reducing properties at ordinary temperature. $PH_3+6AgNO_3+3H_2O=6Ag+6HNO_3+H_3PO_3$
9. Reacts with $CuSO_4$ solution producing deep blue cuprammonium compound.	9. Reacts with $CuSO_4$ solution producing ppt. of copper phosphide.
10. Non-poisonous.	10. Poisonous.

28·9. Oxides of Phosphorus :

Phosphorus forms three oxides having the formulae P_4O_6, phosphorus trioxide ; P_4O_8, phosphorus tetroxide and P_4O_{10}, phosphorus pentroxide. The oxidation number of phosphorus in these compounds are 3, 4 and 5 respsctively.

Phosphorus trioxide P_4O_6 :

Although commonly formulated as monomer, P_2O_3, the compound is dimeric both in solution in benzene and in the vapour state.

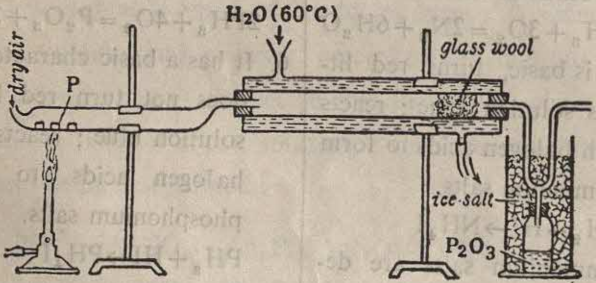


Fig. 28·4. Preparation of P_2O_3

When a slow current of dry air is led over small sticks of white phosphorus kept in a long tube in a slightly warm condition phosphorus trioxide along with some pentoxide are formed. The vapours formed enter into a condenser kept at a temperature of 60°C by circulating hot water. The less volatile P_2O_5 condenses in these tube as a fine powder. There is a plng of glass wool which arrests the last traces of P_2O_5. The more volatile Phosphosrus trioxide passes over and enters into a U-tube cooled by freeting mixture where it condenses (Fig 28·4). If the U-tube is subsquently warmed the trioxide runs out into the small bottle :

$$P_4 + 3O_2 = P_4O_6.$$

Phosphorus trioxide is a colourless crystalline solid with odour of garlic ; m.pt 23·8°C and b.pt 173°C. It is very poisonous and becomes waxy when impure. Phosphorus trioxide undergoes easy oxidation in air or oxygen when heated to phosphorus pentroxide.

In an atmosphere of chlorine it burns spontaneously giving rise to oxy-chloride, $POCl_3$. It is an acidic oxide. With cold water it gives phosphorus acid. But with hot water it produces phosphine and phosphoric acid :

$$P_4O_6+6H_2O=5H_3PO_3 \quad \text{with cold water}$$

$$P_4O_6+6H_2O=PH_3+3PH_3PO_4, \quad \text{with hot water.}$$

It dissolves in many organic solvents like ether, benzene, chloroform etc. without decomposition. Its structure is $O=P—O—P=O$.

Phosphorus tetroxide, P_4O_8 :

It is obtained by heating the trioxide in a sealed tube to 440°C. It is a colourless solid which sublimes in vacuo at 180°C.

$$4P_4O_6 \longrightarrow 6P_2O_4+P_4.$$

It behaves as a mixed anydride since it dissolves in water to yield a mixture of phosphorus and phosphoric acids :

$$P_4O_8+6H_2O=2H_3PO_3+2H_3PO_4.$$

Phosphorus pentoxide, P_4O_{10} :

It is prepared by igniting lumps of white phosphorus in a closed vessel in which excess of dry air is admitted : $P_4+5O_2=P_4O_{10}$. A snow like voluminous mass is formed. It may contain some P_2O_3. It is purified by volatilising in a current of dry air or oxygen. It is stored in air-tight bottles.

It is a white deliquescent solid, which easily sublimes above 250°C. Its vapour density corresponds to the formula P_4H_{10}. When heated under pressure, it melts at 563°C and solidified, on cooling, to a vitreous mass.

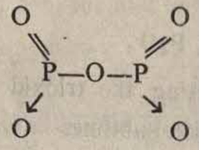
Phosphorus pentroxide is an acidic oxide. It dissolves in cold water with a hissing sound to form metaphosphoric acid at first, which gradually changes into orthophosphoric acid with hot water. Thus it is the anhydride of phosphoric acid.

$$P_4O_{10}+2H_2O=\underset{\text{metaphos-phoric acid}}{4HPO_3}\ ; \qquad HPO_3+H_2O=\underset{\text{ortho phos-phoric acid.}}{H_3PO_4}.$$

It is a powerful dehydrating agent since it has a strong affinity for water. It is capable of extracting water from conc. HNO_3, H_2SO_4 etc. and from alcohol.

$$P_4O_{10}+4HNO_3=4HPO_3+2N_2O_5.$$
$$P_4O_{10}+2H_2SO_4=4HPO_3+2SO_3$$
$$P_4O_{10}+2C_2H_5OH=4HPO_3+2C_2H_4$$

Phosphorus pentoxide is widely used in laboratories as a desiccating agent. Its structure is



Oxy acids of Phosphorus :

Several oxy acids of phosphorus are known of which the principal ones are : phosphorus acid, H_3PO_3 and phosphoric acids (ortho, pyro, and meta phosphoric acids).

28.10. Phosphorus acid, H_3PO_3 :

It is most readily prepared by the acticn of cold water on phosphorus trichloride :

$$PCl_3+3H_2O=H_3PO_3+3HCl.$$

The solution is heated to 180°C to drive off hydrogen chloride and cooled. On cooling the concentrated solution, the acid crystallises out (m. p. 73°C).

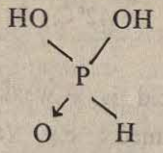
It is a diabasic acid of medium strength and produces two types of salts ; e.g., NaH_2PO_3 and Na_2HPO_3. When heated it decomposes into phosphine and phosphoric acid :

$$4H_3PO_3=PH_3+3H_3PO_4.$$

Phosphorus acid is a powerful reducing agent. It preciditates gold, silver and copper from solution of their salts, and it reduces mercuric chloride to mercurous chloride.

$$H_3PO_3+2AgNO_3+H_2O=H_3PO_4+2Ag+2HNO_3.$$
$$H_3PO_3+CuSO_4+H_2O=H_3PO_4+Cu+H_2SO_4$$
$$H_3PO_3+2HgCl_2+H_2O=H_3PO_4+Hg_2Cl_2+2HCl.$$

The dibasicity of phosphorus acid and its reducing properties are accounted for by the structure :



28.11. Phosphoric acids :

Three phosphoric acids are formed by the addition of water on phosphorus pentoxide, which is therefore, the anhydride of three acids : Ortho phosphoric acid, H_3PO_4 ; pyro phosphoric acid, $H_4P_2O_7$; and metaphosphoric acid, HPO_3.

Ortho phosphoric acid, H_3PO_4 :

(a) It is prepared in the laboratory by refluxing red phosphorus with conc. HNO_3 on a water bath in presence of a trace of iodine (catalyst)

$$P_4 + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2.$$

Brown fumes of nitrogen dioxide is evolved and phosphorus is oxidised to phosphoric acid. At the end of the reaction the liquid is evaporated to a syrupy mass at 170°C. On cooling the latter in a desiccator kept in a freezing mixture, the phosphoric acid separates out as colourless crystals.

(b) On an industrial scale the acid is prepared by digesting bone ash or mineral phosphate with 60% H_2SO_4 ; the mixture is heated for several hours when calcium sulphate and phosphoric acid are formed. The insoluble calcium sulphate is separated by filteration, and the solution of phosphoric acid is concentrated by evaporation.

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

(c) Now-a-days, in some cases, the phosphorus vapour obtained in Parker-Robinson process is directly oxidised by mixing with oxygen to P_2O_5. It is then transformed into phosphoric acid by dissolving in warm water.

Properties : (i) Orthophosphoric acid, generally called phosphoric acid, is a colourless syrupy liquid which on cooling, gives colourness crystalls. melting at 42°C. It is highly soluble in water.

(ii) Ortho phosphoric acid is a weak tribasic acid and hence three series oi salts are formed : e.g. (a) Primary phosphate, NaH_2PO_4 ; (b) Secondary phosphate, Na_2HPO_4 ; (c) Tertiary phosphate, Na_3PO_4.

(iii) The alkali primary phosphate, reacts acidic to litmus solution :

$$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4^- \ ; \ H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--}.$$

The secondary phosphate is very faintly alkaline and the tertiary phosphate strongly alkaline, since they are hydrolysed by water :

$$Na_2HPO_4 + H_2O \rightleftharpoons NaH_2PO_4 + NaOH.$$
$$Na_3PO_4 + H_3O \rightleftharpoons Na_2HPO_4 + NaOH.$$

(iv) when heated to 213°C ortho phosphoric acid (H_3PO_4) slowly transformed into pyrophoric acid ($H_4P_2O_7$) by losing water which in turn is converted to metaphosphoric acid (HPO_3) by dehydration on further heating to 316°C. Ultimately at red heat, metaphosphoric acid changed to P_2O_5. The transformations are reversible.

$$2H_3PO_4 \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} H_4P_2O_7 \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} 2HPO_3 \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} P_2O_5$$

(v) The primary and secondary phosphates decompose on heating with elimination of water, tertiary phosphate remains unchanged by heat.

$$\underset{\text{(primary phosphate)}}{NaH_2PO_4} = H_2O + \underset{\text{(metaphosphate)}}{NaPO_3}$$

$$2Na_2HPO_4 = H_2O + Na_4P_2O_7$$

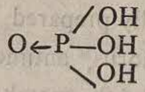
(secondary phosphate) (pyrophosphate)

Phosphates containing ammonium radicals, lose both water and ammonium on heating ;

$$(NH_4)_2HPO_4 = HPO_3 + H_2O + 2NH_3.$$
$$2MgNH_4PO_4 = Mg_2P_2O_7 + H_2O + 2NH_3.$$

Uses : Phosphoric acid is required in preparation of fertilisers and some salts. Syrupy phosphoric acid is used as a dehydrating agent. Salts of different phosphoric acids are used in dyeing, in water softening, in baking powders, in medicine etc.

The molecular structure of orthophosphoric acid is respected as—



28·12. Test for phosphoric acid and phosphates :

A small ammount of ortho phosphoric acid or any of its salt when treated with exces conc. HNO_3 and ammonium molybdate solution would produce a beautiful canary-yellow precipitate of ammonium phospho-molybdate.

28·13. Superphosphate of lime :

Phosphate fertilisers are essential for the soil for crop production. Naturally occurring phosphatic minarals can be used as good fertiliser as they are not readily soluble. The most commonly used phosphate fertiliser is "superphosphate of lime".

Equal quantities of chamber sulphuric acid (65 to 70% H_2SO_4) and powdered phosphorite rock or apatite are run into a cast iron mixture, with a mechanical stirrer. The whole mass is thoroughly mixed. The mixture is then quickly dumped in a closed pit for 24 hours to complete the reaction. The temperature rises to about 100°C. Some gases HCl, CO_2, SiF_4 etc. are evolved which escape through a vent in the pit. Finally a mixture of monocalcium phosphate and calcium sulphate is formed, which is called *superphosphate of lime.* It is taken out of the pit and allowed to mature for 2 months before it is ready for use in the soil. The reaction may be represented as :

$$Ca_3(PO_4)_2+2H_2SO_4+4H_2O=Ca(H_2PO_4)_2+2(CaSO_4, 2H_2O)$$

28·14. Manufacture of matches :

One of the most important uses of phosphorus is in match industry. Red phosphorus and phosphorus sulphide are used for the purpose—the uses of yellow phosphorus (previously used for lucifer matches) is prohibited by law, due to its poisonous nature.

Safety matches : The match sticks are tipped with a paste containing potassium chlorate, MnO_2 sulphur, potassium dichromate powdered glass, gum and glue, bnt no phosphorus. The sticks are ignited on rubbing on a specially prepared surface made by pasting a paper coated with red phosphorus, antimony sulphide, powdered glass and glue, on the two sides of the match box. The heat of friction brings about the oxidation of phosphorus by $KClO_3$—the spirk being communicated to the sticks which ignite. The stick is often impregnated with borax, so that it does not glow after the same is blown ont.

28·15. Comparison of nitrogen and phosphorus :

Both nitrogen and phosphorus belong to the same group (group-V) of the periodic table, hence it is expected that they shouled possess similar properties. The difference is only in degree not in kind. Some of their properties are compared here :

(1) Both the elements are non-metals. At the ordinary temperature nitrogen is gaseous whereas phosphorus is a solid.

(2) Nitrogen moleculs are diatomic, having the formula N_2. Phosphorus molecules are tetratomic (P_4).

(3) The electronic configurations of the atoms of nitrogen and phosphorus are as follows :

N-atom······$1s^2 2s^2 2p^3$; P-atom······$1s^2 2s^2 2p^6 3s^2 3p^3$.

Both the elements have five electrons in their outer shell and both exhibit variable valencies with a maximum valency of five.

Valencies : Nitrogen ; $\overset{3}{N}H_3$, $\overset{5}{N}_2O_5$ Phosphorus ; $\overset{3}{P}H_3$, $\overset{5}{P}_2O_5$.

(4) Nitrogen exist in two forms, ordinary nitrogen and active nitrogen ; phosphorus has two principle allotropes : white and red phosphorus.

(5) Nitrogen is less reactive than phosphorus, hence nitrogen occur in nature in the free state whereas phosphorus does not. This difference in reactivity is due to the fact that in nitrogen molecule, two atoms are linked with a triple bond and the bond energy is very

high. more energy will be required to rupture the bond. Where as in tetraatomic phosphorus molecule, the atoms are linked with single bonds in the form a tetrahedron and hence rupture of the bond is easier.

(6) Both nitrogen and phosphorus give same type of hydrides with similar properties :

Nitrogen—NH_3, N_2H_4 Phosphorus—PH_3, P_2H_4.

(7) Both nitrogen and phosphorus produce a number of oxides and oxyacids with more or less similar behaviours.

	oxides	*oxyacids*
Nitrogen :	N_2O, NO, N_2O_3, N_2O_4, N_2O_5	HNO_2, HNO_3
Phosphorus -	P_2O_3, P_2O_4, P_2O_5	H_3PO_3, H_3PO_4, HPO_3

(8) Both the elements form unstable chlorides which are easily hydrolysed : $NCl_3+3H_2O=NH_3+3HOCl$; $PCl_3+3H_2O=H_3PO_3+3HCl$

(9) Both nitrogen and phosphorus form binary compounds with metals yielding nitrides and phosphides. These binary metallic compounds are hydrolysed by heating with water producing NH_3 and PH_3.

$$Ca_3N_2+6H_2O=3Ca(OH)_2+2NH_3$$
$$Ca_3P_2+6H_2O=3Ca(OH)_2+2PH_3$$

(10) Both the elements are important constituents in the preparation of fertilisers.

Exercise—28

1. Name the principal allotropes of phosphorus and compare their characteristic properties. How can they be inter-converted ?

2. How is white phosphrous produced on a large scale ? Why is this element more reactive than nitrogen ? Mention the important uses of phosphorus.

3. (i) Starting from white phosphorus, how would you prepare :—
   (a) meta phosphoric acid, (b) ortho phosphoric acid, (c) red phosphorus and (d) phosphine.
   (ii) Discuss the action of white phosphorus on (a) nitric acid, (b) copper sulphate solution, (c) chlorine and (d) caustic soda.

4. How would you prepare phosphine in the laboratory ? Illustrate its reducing property with examples. Compare its properties with those of ammonia.

5. How is phosphorus pentoxide prepared ? What are its uses ? Discuss the action of water on phosphours trioxide and pentoxide,

6. How would you prepare anhydrous phosphoric acid from phosphatic rock ? How can you obtain phosphorus from phosphoric acid ? Discuss the action of heat on phosphoric acid.

7. Give the names with formula the different calcium salts of phosphorus acid and phosphoric acid. How do you identify the presence of phosphate in a given sample ?

8. Write notes on :—

(a) the glow of phosphorus, (b) superphosphate of line, (c) safety matches, (d) phosphorus trioxide and (e) allotrpes of phosphorus.

CHAPTER XXIX

SULPHUR

Atomic number 16, Atomic weight 32·06, Electronic Configuration $1s^2 2s^2 2p^6$-$3s^2 3p^4$. Atomicity S_8,

29·1. History and occurrence :

The element sulphur has been known to the ancient Greeks and Romans who were familiar with the use of the element. Sulphur has assumed importance since pre-historic time in the development of chemistry.

Sulphur occurs in nature both in the free and the combined states. Deposits of free sulphur occur in the volcanic regions of Sicily, Italy and Japan. The greatest source of sulphur is in Louisiana and Texas in U. S. A.—which produce about 80 per cent of the world's supply.

In the combined state, sulphur exists in nature mostly as sulphides and sulphates. The chief sulphide minerals are : *iron pyrites* FeS_2, *copper pyrites* $CuFeS_2$, *galena* PbS, *Zinc blende* ZnS *cinnabar* Hgs, etc. The principal naturally occuring metallic sulphates are *gypsum* $CaSO_4$, $2H_2O$, *Kieserite* $MgSO_4$, H_2O, *heavy spar* $BaSO_4$, etc. Sulphur is present in coal in small quantities. It is also present in plant and animal tissues ; nearly 0·25% of human body is made up of sulphur.

29·2. Production of sulphur :

Most of our sulphur requirment is met from the native deposits in U. S. A. and in Sicily. The methods followed for production in the two places are, however different.

(a) *Sicilian Process* : The sulphur deposits in Sicily are practically on the surface and contain about 20 per cent of free sulphur. The sulphur bearing rock is mechanically removed and dumped in big masonary furnaces with slopping floors. The sulphur is separated from the rock by liquation. The charge is ignited at one end and nearly one-third of the sulphur is allowed to burnt away. The heat produced melts the rest of the sulphur which flows down the sloping floor of the kiln and collects in large wooden vats, leaving behind the stones and other impurities. The crude sulphur still contains about 5% rocky impurities. The efficiency of the process is increased by using four or six of such sulphur kilns which are inter connected so that the hot gases may pass from one to the other kiln and the waste heat is thus utilised. This is called the *Gill process*. At first sight the precess appears wasteful, but native sulphur is cheaper than imported coal.

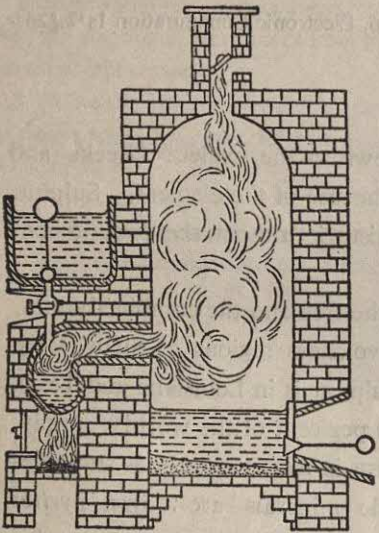


Fig. 29·1. Sicilian process

The crude sulphur is conveyed to Marseilles in France where it is refined by distillation. There it is distilled from big iron retorts in arge brick work chambers (Fig 29·1). The sulphur which condenses on the cold brick walls as a yellow solid at the begining of the distillation is known is *flowers of sulphur*. As the chambers grow warmer, the vapour condenses to liquid sulphur which collects at the bottom, whence it is tapped out and cast in moulds to from *roll sulphur*.

(b) *The American or Frasch Process* : The sulphur deposits in U. S. A. are at a depth of 600 ~ 1100 feet and contain about 70 ~ 75% of sulphur. The deposit is surrounded by layers of limestone, quicksands and clay. The quick-sands make

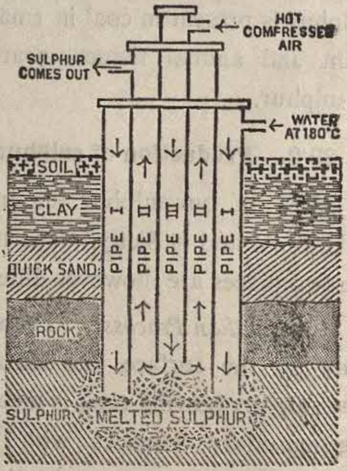


Fig. 29·2. Frasch Proeess

ordinary mining impossible. According to Frasch process, boring is made to reach the sulphur deposit and three concentric pipes are sunk—the diameter of the outermost pipe is 8 inches (Fig 29·2), Super-heated water at about 180°C and under a pressure of 10—18 atmospheres is forced down the outer pipe (pipe I). This melts the sulphur. Through the central innermost pipe (pipe III) is forced down air under pressure. This air produces a foamy emulsion of molten sulphur, water and air below which is forced up through the middle pipe (pipe II). The outcomming sulphur is led into pans, water is distilled off and sulphur solidifies as practically 99 9% pure sulphur and is ready for immediate use.

Recovered sulphur :

Two important sources are (i) the hydrogen sulphide distilled from coal in the manufacture of coal gas, which is recovered as sulphur from spent iron oxide in the purifiers, and (ii) the sulphur dioxide liberated during the roasting of sulphide ores of copper, lead, zinc etc. and during the burning of coal at large power stations. The sulphur dioxide is concentrated and then reduced by coke at 1100°C : $SO_2 + C = CO_2 + S$.

29·3. Allotropy of Sulphur :—Sulpur exhibits the largest number of allotropic forms among the elements. It has allotropic forms both in the solid state as well as in the liquid state.

(a) In the solid state the two common crystalline forms are : (i) rhombic or α-sulphur ; (ii) monoclinic or β-sulphur, and the three amorphous forms are : (i) plastic or γ-sulphur, (ii) milk of sulphur (iii) colloidal sulphur. (b) In the liquid state, sulphur exists in three allotropic forms, namely : (i) Lambda sulphur, S_λ, (ii) Pi-$_{\iota}$,-sulphur, S_π, (iii) Mu-sulphur, S_μ,

All the various forms of sulphur possess more or less identical chemical properties, but there is considerable variation in their physical properties.

Rhombic Sulphur, $S\alpha$: It is the most stable form of sulphur at ordinary temperatures, other forms are slowly transformed into α-sulphur on keeping. It is best prepared by the evaporation of a solution of roll sulphur in carbon disulphide. Transparent lemonyellow orthorhombic crystals (Fig 29.3) are deposited. Its density is 2·06 gm/c.c. and if it is heated continuously and rapidly it would melt at 112·8°C. But if it is heated and kept at a temperature of 95·6°C, or slightly above, α-sulphur will be transformed into β-sulphur. α-sulphur is freely soluble in CS_2, but in soluble in water. Its molecule is composed of eight atoms which are bound together in a closed ring (Fig 29.4).

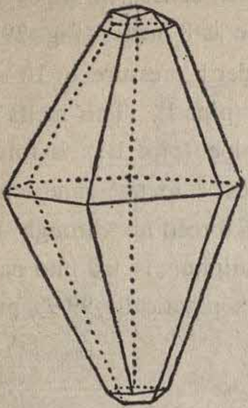


Fig. 29·3. Rhombic sulphur crystal

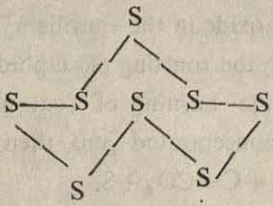


Fig. 29·4. S_8 molecule

Monoclinic Sulphur, $S\beta$:—Monoclinic sulphur exists as a dark yellow needle like crystals at a temperature above 95·6°.C If α-sulphur be heated and kept at a temperature above 95·6°C, it slowly changes into the β-variety. That is, above 95·6°C β-sulphur is stable and below 95·6°c α-sulphur is stable. At 95·6°C, both the varieties of sulphur cc-exist in equilibrium : $S_\alpha \overset{95\cdot6^\circ C}{\rightleftharpoons} S_\beta$, and this temperature is called the *transition temperature* of sulphur. The phenomenon in which different allotropic forms of an element are stable at different ranges of temperature is known as *Enantiotropism.* Monoclinic sulphur is prepared by

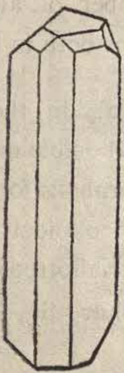
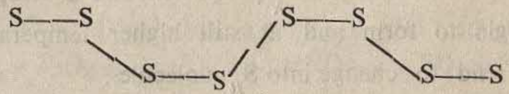


Fig. 29·5. Monoclinic Sulphur crystal

melting rhombic sulphur in a crucible at about 120° ~ 130°C and cooling it slowly till a solid crust is formed on the surface. The crust is pierced at two points and the still liquid sulphur is poured out. On removing the crust, the crucible will be found to be lined with needle-shaped amber-yellow crystals of monoclinic sulphur (Fig 29.5). Its density is 1·96 gm/c.c . and also soluble in CS_2. β-sulphur melts at 119°C. This variety also forms S_8-molecules.

Plastic Sulphur :—It is also called γ-sulphur. It is prepared by heating sulphur nearly to its boiling point and then pouring the black mobile liquid sulphur into cold water in thin stream whereby it solidifies to rubber-like elastic transparent yellow strings of plastic or γ-sulphur. It is amorphous, sp.gr. 1·92 and insoluble is CS_2, as it contains mostly $S\mu$ (see liquid sulphur). It passes into rhombic form on standing. Plastic sulphur consists of chains of sulphur atoms and hence it can be stretched.



Colloidal Sulphur :—A milky colloidal suspension of amorphous sulphur is obtaiaed (i) when a dilute solution of sodium thiosulphate is acidified or (ii) by passing hydrogen sulphide into a solution of sulphur dioxide at low temperature or (iii) when an alcoholic solution of α-sulphur is poured into a large mass of water.

$$Na_2S_2O_3 + 2HCl = 2NaCl + S + SO_2 + H_2O$$

$$2H_2S + SO_2 = 2H_2O + S.$$

The colloidal sulphur sol may have variety of colour depending on the size of the sulphur particles: Some forms of colloidal sulphur are soluble in CS_2, while some other forms are insoluble.

Milk of Sulphur : This is a variety of white amorphous sulphur. When a suspension of powdered sulphur and milk of lime is boiled, an orange coloured liquid is formed. The liquid is separated by filtration and acidified with HCl when milk of sulphur is formed.

$$12S + 3Ca(OH)_2 = 2CaS_5 + CaS_2O_3 + 3H_2O$$
$$2CaS_5 + CaS_2O_3 + 6HCl = 3CaCl_2 + 12S + 3H_2O.$$

Milk of sulphur is soluble in CS_2.

29·4. Effect of heat on Sulphur : Liquid Sulphur :—When powdered solid sulphur is heated, the yellow colour deepens and then turns brown. It then melts into an amber-coloured mobile liquid at about 113°C. This molten sulphur undergoes a series of remarkable changes when it is heated slowly to its boiling point. On heating the mobile yellow liquid deepens into a dark red liquid and at about 160°C the mobility decreases, it becomes a viscous mass. On further heating, the mobility is lost and the liquid becomes very dark and viscous at 230°C. At about 300°C, the liquid still remains dark but the mobility is regained and it changes into a mobile liquid. Finally it boils at 444 6°C. At the boiling point the liquid is almost black. These changes are due to the presence of three forms of sulphur, S_λ, S_π and S_μ in the liquid state, which are in dynamic equilibrium. Just on melting, it contains only the allotrope S_λ, but with rise in temperature S_π molecules begin to form and at still higher temperature, some S_π molecules tend to change into S_μ molecules.

$$S_\lambda \xrightleftharpoons{120^\circ \sim 170^\circ} S_\pi \xrightleftharpoons{170^\circ \sim 444{\cdot}6^\circ} S_\mu$$

S_λ with molecular composition S_8 is yellow and soluble in CS_2 at room temperature ; S_π with molecular constitution S_4 is red and dissolves in CS_2 at all temperatures ; S_μ with unknown molecular composition is insoluble in CS_2.

When vapours of sulphur are allowed to come in contact with very cold surface, small puffs of white coloured sulphur deposit. These are called *Flowers of sulphur.* These are not crystalline and are mostly S_μ.

29·5. Properties of sulphur : (i) Sulphur is a pale yellow brittle solid which exists in several allotropic modifications. The different forms melt at different temperatures, but the liquid sulphur produced from any modification boils at a definite temperture of 444·6°C. This temperature is used as a fixed point in thermometry.

The density and solubility of its different forms have been mentioned earlier. Sulphur vapour contains mainly S_8 and S_2 molecules in equilibrium :

$$S_8 \rightleftharpoons 4S_2.$$

(ii) Sulphur is an inflammable substance. It burns in oxygen or air with a blue flame giving sulphur dioxide and a little sulphur trioxide.

$$S+O_2=SO_2\ ;\ \ 2SO_2+O_2=2SO_3.$$

(iii) When heated, sulphur unites directly with hydrogen, the halogens (except iodine), carbon, phosphorus, and also with most metals, forming sulphides.

$$2S+Cl_2=S_2Cl_2 \qquad P_4+10S=2P_2S_5$$
$$C+2S=CS_2 \qquad Fe+S=FeS$$
$$H_2+S=H_2S \qquad Hg+S=HgS.$$

(iv) Hot concentrated sulphuric and nitric acids slowly oxidise sulphur to sulphur dioxide and to sulphuric acid respectively :

$$S+2H_2SO_4=3SO_2+2H_2O\ ;\ \ S+6HNO_3=H_2SO_4+6NO_2+2H_2O.$$

(v) Sulphur dissolves in alkalis to yield primarily a mixture of sulphide and sulphite, thus :

$$3S+6KOH=2K_2S+K_2SO_3+3H_2O$$

Both the sulphide and the sulphite dissolve sulphur to form respectively polysulphides such as K_2S_2,K_2S_4, and thiosulphate, $K_2S_2O_3$ and these compounds will therefore be present in the solution. If sulphur is boiled with a suspension of slaked lime a reddish yellow liquid is obtained containing calcium pentasulphide and thiosulphate :

$$12S+3Ca(OH)_2=2CaS_5+CaS_2O_3+3H_2O.$$

(vi) If a mixture of sulphur and potassium carbonate is fused a brown mass called *liver of sulphur* is produced :

$$6S+3K_2CO_3=2K_2S_2+K_2S_2O_3+3CO_2.$$

29·6. Uses of sulphur : (i) Sulphur is largely used for the manufacture of sulphuric acid and for the preparation of bisulphite for paper manufacture. (ii) Sulphur is also used for making carbon disulphide, sulphur chloride, ultramarine, sodium thiosulphate, dyes and in vulcanising rubber. (iii) Free sulphur is present in gunpowder, matches, and fireworks. (iv) Colloidal sulphur is used in medicine, it is also used as a fungicide in agriculture,

29·7. Identity of allotropes of sulphur :—All the different forms of sulphur are chemically identical and all of them are one and the same element sulphur. This can be proved as follows :—

(a) The various forms of sulphur are inter-convertible. All the different forms of sulphur are transformed to Rhombic sulphur on keeping at room temperatures.

(b) The identity of different allotropes may be establisted by igniting equal weights (say 1 gm) of the different forms in oxygen, when the same weight of sulphur dioxide is obtained in all cases :

$$S+O_2=SO_2.$$

(c) A better method is to oxidise equal weights of different forms of sulphur to sulphuric acid by heating with fuming nitric acid and precipitate the sulphuric acid formed as barium sulphate ; the precipitate is filtered, washed, dried and weighed. The same weight of barium sulphate is obtained in all cases.

COMPOUNDS OF SULPHUR

Sulphur forms compounds in which it can behave either as a bivalent, tetravalent or hexavalent element. The compounds may be covalent or ionic. Sulphur combines with hydrogen to produce several hydrides of which the important is hydrogxn sulphide, H_2S also called sulphuretted hydrogen.

HYDROGEN SULPHIDE, H_2S

29·8. Occurreace : Hydrogen sulphide occurs in some volcanic gases, in many spring water and in decaying organic substances which contain sulphur such as, rotten fishes or eggs, etc. Air contains traces of the gas which causes silver objects to tarnish.

29·9. Preparation : (i) Hydrogen sulphide is generally prepared in the laboratory by the action of cold dilute sulphuric acid upon pieces of ferrous sulphide taken in a Woulfe's bottle fitted with a thistle funnel and a delivery tube. The evolved hydrogen sulphide gas is washed by passing through a small quantity of water and collected over hot water, if it is not required dry. It may be dried with fused calcium chloride or phosphorus pentoxide and collected by the upward displacement of air (Fig 29.6) as the gas is heavier then air : $FeS+H_2SO_4=FeSO_4+H_2S$. The gas cannot be dried with conc. H_2SO_4 as it reacts with H_2S.

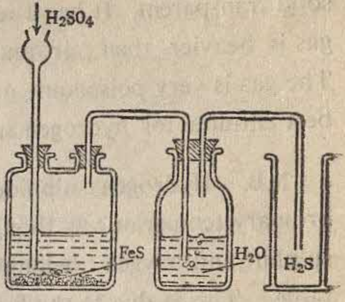


Fig. 29·6. preparation of hydrogen sulphide

$$H_2SO_4+H_2S=2H_2O+SO_2+S$$

For ready supply of the gas in the laboratory, kipp's apparatus is always used.

The gas thus produced contain some hydrogen, for the iron sulphide used in its preparation always contains some iron in it. The gas may be separated from hydrogen by passing through a U-tube cooled with solid carbondioxide, when H_2S liquefies and hydrogen passes out. Gaseous H_2S can then be obtained by warming the liquid.

(ii) Hydrogen sulphide free from hydrogen may be obtained by the action of hot concentrated hydrochloric acid on antimony sulphide. The gas is dried by passing over P_2O_5 and then collected by the displacement of air or over dry mercury :

$$Sb_2S_3+6HCl=2SbCl_3+3H_2S.$$

(iii) The purest hydrogen sulphide is prepared by passing a mixture of sulphur vapour and hydrogen over finely divided nickel heated to 450°C ;

$$H_2+S=H_2S.$$

29·10. Properties : (i) Hydrogen sulphide is a colourless gas, B. pt. −60·4°C, M. pt. −85·6°C, the liquid is colourless and the solid transparent. It has a repulsive smell like that of rotten egg. The gas is heavier than air and is moderately soluble in cold water. The gas is very poisonous at concentrations above 0·1 percent. The best antidote for hydrogen sulphide poisonsng is dilute chlorine.

N.B. Hydrogen sulphide is a gas, whereas water is a liquid at ordinary temperatures, though they are the hydrides of the elements sulphur and oxygen, belonging to the same group of the periodic table. This is due to the fact that water molecules remain frequently associated due to hydrogen bonding (chapter 16) and at ordinary temperatures, water is a liquid consisting largely of trimeric molecules, $(H_2O)_3$. But hydrogen sulphide molecules are not associated and at ordinary temperatures, it is a gas composed of simple molecules, H_2S.

(i) Hydrogen sulphide does not support combustion but it itself burns in excess air or oxygen with a blue flame, producing water and sulphurdioxide ;

$$2H_2S+3O_2=2H_2O+2SO_2$$

but sulphur is deposited, if the supply of oxygen is limited :

$$2H_2S+O_2=2H_2O+2S.$$

Hydrogen sulphide breaks up into its elements when heated above 600°C :

$$H_2S=H_2+S.$$

(iii) The aqueous solution of hydrogen sulphide is a weak dibasic acid, turns blue litmus red. Two types of salts, sulphides and hydrosulphides , are formad by it on reaction with alkalis.

$$H_2S+NaOH=NaHS+H_2O\ ;\ H_2S+2NaOH=Na_2S+3H_2O.$$

The solution of hydrogen sulphide becomes turbid when kept exposed to air due to the separation of sulphur by atmospheric oxidation :

$$2H_2S+O_2=2H_2O+2S$$

(iii) It attacks many metals directly converting them into their sulphides. Gold and platinum are not attacked.

$$2Ag+H_2S=Ag_2S+H_2\;;\qquad Hg+H_2S=Hg_2S+H_2$$
$$Ni+H_2S=NiS+H_2\;;\qquad Sn+H_2S=SnS+H_2$$

The silver and nickel watches turn black in chemical laboratories due to the attack of sulphuretted hydrogen.

(iv) Hydrogen sulphide is good reducing agent because of the ease with which it decomposes into hydrogen and sulphur. Thus it reduces halogens to correrponding hydracids ; in acid solutions permanganates are reduced to manganous salts—the pink colour of the solution is thereby discharged ; dichromates to chromic salts—the orange red colour of the solution turns green ; and ferric salts are reduced to ferrous salts, the yellow colour of the solution thus turns colourless. Hydrogen peroxide is reduced to . water. Hydrogen sulphide reduces sulphur dioxide in presence of moisture. Concentrated sulphuric acid and nitric acids are reduced to sulphur dioxide and nitrogen peroxide respectively. In such reactions always sulphur is formed from hydrogen sulphide.

$$H_2S+Cl_2=2HCl+S\;;\; H_2S+Br_2=2HBr+S\;;$$
$$2KMnO_4+3H_2SO_4+5H_2S=K_2SO_4+2MnSO_4+8H_2O+5S\;;$$
$$K_2Cr_2O_7+4H_2SO_4+3H_2S=K_2SO_4+Cr_2(SO_4)_3+7H_2O+3S\;;$$
$$2FeCl_3+H_2S=2FeCl_2+2HCl+S\;;$$
$$H_2O_2+H_2S=2H_2O+S\;;\; SO_2+H_2S=2H_2O+S\;;$$
$$H_2SO_4+H_2S=2H_2O+SO_2+S\;;$$
$$2HNO_3+H_2S=2H_2O+2NO_2+S.$$

In certain cases with excess of oxidising agent, e.g., with Cl_2 or HNO_3, sulphur is further oxidised to sulphuric acid :

$$H_2S+4H_2O+4Cl_2=H_2SO_4+8HCl.$$

(v) *Precipitation of metallic sulphides* : When hydrogen sulphide is passed into solution of metallic salts, precipitates of the corresponding sulphides are often formed. These sulphides can often be identified by their distinct colour or solubility in acids. Thus, many sulphides are precipitated from solutions acidified with dilute hydrochloric acid—copper, lead, mercury and bismuth salts, all give *black* sulphides ; cadmium and arsenic give *yellow* sulphides ; antimony, an *orange-yellow* sulphide ; and tin salts (stannous) give a brown sulphide.

$CuSO_4+H_2S=CuS+H_2SO_4$; $Cd(NO_3)_2+H_2S=CdS+2HNO_3$;
$HgCl_2+H_2S=HgS+2HCl$; $2SbCl_3+3H_2S=Sb_2S_3+6HCl$.

The sulphides of zinc (white), manganese (flesh coloured), iron. cobalt and nickel (all black) are precipitated in ammoniacal (alkaline) medium and only partially in neutral solutions :

$ZnSO_4+H_2S=ZnS+H_2SO_4$; $FeSO_4+(NH_4)_2S=FeS+(NH_4)_2SO_4$

The sulphides of alkali metals are soluble in water. The sulphides of alkaline earth metals are sparingly soluble, but they react with water giving soluble hydrosulphides : $2CaS+2H_2O=Ca(HS)_2+Ca(OH)_2$. Hence these are not obtained as precipitates when H_2S is passed into their salt solution. Aluminium and chromium sulphides are decomposed by water forming the hydroxide : $Al_2S_3+6H_2O=2Al(OH)_3+3H_2S$. and so these are also not available as precipitates.

29·11. Uses : Hydrogen sulphide is sometimes used as a reducing agent in the laboratory, but its use as an analytical reagent in qualitative analysis is most important. It is chiefly used in chemical laboratories for detection, classification and separation of certain metals.

(i) many metals may be identified from the distinctive colours of their sulphides, which are formed when H_2S is passed through the metallic salt solutions. This has already been discussed.

(ii) Hydrogen sulphide helps in classifying the metals into different analytical groups according to the solubitity of their sulphides in water, acid and alkali.

(a) Metals whose sulphides are insoluble in water and in dilute mineral acids e.g., copper, lead, mercury, cadmium, tin, antimony etc. belong to Gr II (A & B).

(b) Some sulphides (those of zinc, manganese, nickel etc.) are soluble in acids but insoluble in alkaline medium and hence these are precipitated in ammoniacal solutions. These metals belong to Gr III B.

(c) Metals whose sulphides are soluble in water, e.g., sodium, potassium etc., which are not precipated at all by H_2S, belong to Gr V.

(iii) Hydrogen sulphide is very helpful in separating metals of different groups from their solution. Thus, when hydrogen sulphide is passed through a hot acidified (with dil. HCl) solution containing copper, zinc and potassium salts (say sulphates), only copper is precipitated as black cupric sulphide. After complete precipitation, cupric sulphide is separated by filtration. The filtrate is made alkaline by adding ammonia and H_2S is passed through this ammoniacal solution, when white zinc sulphide is precipipated. Sufficient H_2S is passed to complete the precipitation and zinc sulphide is separated by filtration, the filtrate now contains potassium salt in solution. Thus the three salts are separated.

Tests :—The presence of hydrogen sulphide may be recognised (i) by its smell of rotten egg, (ii) by its turning lead acetate paper black due to the formation of lead sulphide : $Pb(CH_3COO)_2+H_2S=PbS+2CH_3COOH$, (iii) by the production of a purple colouration in alkaline sodium nitroprusside solution :

$$\underset{\text{(sodium nitroprusside)}}{Na_2S+Na_2[FeNo(CN)_5]}=Na_4[Fe(CN)_5NOS].$$

29·12. Composition of hydrogen sulphide : Some copper turnings are taken in a wide glass tube. It is closed at both ends with

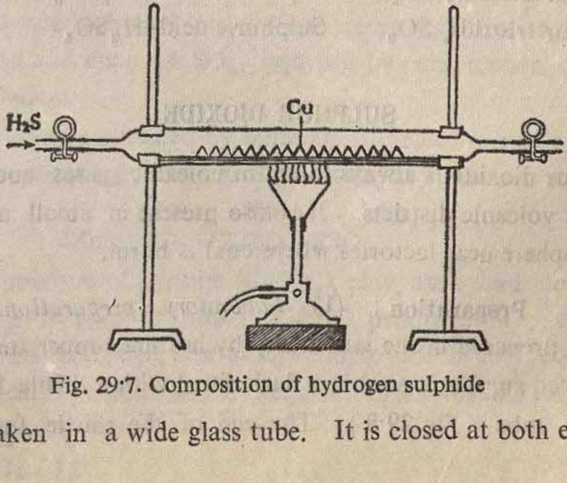


Fig. 29·7. Composition of hydrogen sulphide

ings are taken in a wide glass tube. It is closed at both ends with rubber-tubes and clips. The tube is filled with dry H_2S gas at atmospheric pressure. It is then heated for sometime when cuprous sulphide is formed along with hydrogen.

$$2Cu + H_2S = Cu_2S + H_2$$

The heating is stopped and when the apparatus cools to room temperature, one end of the tube is opend under mercury, the mercury does not enter nor any gas comes out. That is, *hydrogen sulphide contains its own volume of hydrogen.*

Hence x volumes of hydrogen sulphide contain x vols of hydrogen. or, n molecules of hydrogen sulphide contain n molecules of hydrogen (by Avogadros' Hypothesis)

i.e. 1 molecule of hydrogen sulphide contains 1 molecule of hydrogen or 2 atoms of hydrogen

Let the molecular formula of hydrogen sulphide be H_2S_x.

Its vapour density is 17, hence molecular weight $= 2 \times 17 = 34$.

$\therefore$ $2 \times 1 + x \times 32 = 34$ or $x = 1$. i.e. the formula of hydrogen sulphide is H_2S.

OXIDES AND OXYACIDS OF SULPHUR

There are a number of oxides and oxyacids of sulphur. Two important oxides of sulphur with their corresponding oxyacids are :

Oxides	Oxyacids	oxidation state
Sulphur dioxide, SO_2	Sulphurous acid, H_2SO_3	+4
Sulphur trioxide, SO_3	Sulphuric acid, H_2SO_4	+6

SULPHUR DIOXIDE

Sulphur dioxide is always found in volcanic gases and in some springs of volcanic districts. It is also present in small amounts in the atmosphere near factories where coal is burnt.

29·13. Preparation : (1) *Laboratory preparation.* Sulphur dioxide is prepared in the laboratory by heating copper turnings with concentrated sulphuric acid in a flask fitted with a thistle funnel and a delivery tube (Fig 29·8). The end of the thistle funnel dipps under the acid. When heated, sulphur dioxide is evolved with effervescence. The gas comes out through the delivery tube and is collceted by upward displacement of air :$Cu+2H_2SO_4=CuSO_4+2H_2O+SO_2$ The gas produced may be contaminated with traces of H_2S which may be removed by bubbling the gas through lead acetate sotlution. It may be dried by conc. H_2SO_4, and collected over mercury.

Concentrated sulphuric acid may also be reduced by similarly boiling the acid with silver, mercury, carbon or sulphur.

$2Ag+2H_2SO_4=Ag_2SO_4+2H_2O+SO_2$;
$Hg+2H_2SO_4=HgSO_4+2H_2O+SO_2$;
$C+2H_2SO_4=CO_2+2H_2O+SO_2$;
$S+2H_2SO_4=3SO+2H_2O$.

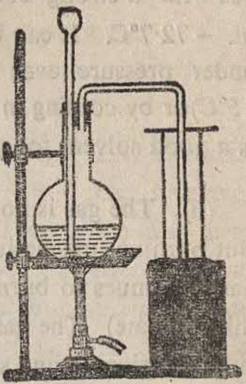


Fig. 29·8. Preparation of sulphur dioxide

(2) An instantaneous and ready supply of sulphur dioxide in the laboratory often made by dropping conc. H_2SO_4 on a saturated solution of sodium bisulphite

$$NaHSO_3+H_2SO_4=NaHSO_4+H_2O+SO_2.$$

(3) *Industrial preparation* : on the industrial scale, sulphur dioxide is made by burning sulphur in air : $S+O_2=SO_2$. The gaseous products of combustion pass up a tower to meet a descending stream of cold water which dissolves out the sulphur dioxide. The sulphur dioxide is boiled out of the resulting solution, dried by refrigeration and conc. H_2SO_4, liquefied by compression, and stored in steel cylinders.

It may also be obtained by roasting sulphide minerals, such as iron pyrites, copper pyrites and znic blende, or spent iron oxide.

$$4FeS_2+11O_2=2Fe_2O_3+8SO_2 ;$$
$$2ZnS+3O_2=2ZnO+2SO_2.$$

(4) A mixture of gypsum ($CaSO_4$), clay, sand and coke, when heated in a furnace at about 1200°C, produces SO_2 along with cement. This method is now-a-days employed in our country for the large scale production of sulphur dioxide for the manufacture of sulphuric acid.

29·14. Properties :—(i) Sulphur dioxide is a colourless, heavy gas with a strong suffocating smell, boiling point $-10°C$, melting pt. $-72{\cdot}7°C$. It can be easity liquefied to a colourless, heavy liquid under pressure even at ordinary temperature (2·5 atmospheres at 15°C)or by cooling in a freezing mixture. The liquid sulphur dioxide is a good solvent for sulphur, phosphorus, iodine and resins.

(ii) The gas is not combustible nor a supporter of combustion. But burning magnesium of potassium, when introduced into the gas, continues to burn : $4K+3SO_2=K_2SO_3+K_2S_2O_3$ (potassium thiosulphate) The gas itself is quite stable. It decomposes into sulphur trioxide and sulphur, when heated to a high temperature : $3SO_2 \rightleftharpoons 2SO_3+S$.

(iii) Sulphur dioxide is highly soluble in water—the solution smells strongly of the gas, which can be removed from its solution by boiling. The aqueous solution is acidic, turning blue litmus red, due to the formation of unstable sulphurous acid : $H_2O+SO_2=H_2SO_3$. Hence, sulphur dioxide is the *anhydride* of sulphurous acid. The acid, however, cannot be isolated in the free state. It is dibasic and forms two series of salts, bisulphites (eg. $NaHSO_3$) and sulphites (e.g. Na_2SO_3).

(iv) *An acidic oxide*, it is absorbed by aikalis, forming sulphites and bisulphites :

$NaOH+SO_2=NaHSO_3$; $NaHSO_3+NaOH=Na_2SO_3+H_2O$.

Sodium carbonate solution reacts similarly with SO_2 :

$$Na_2CO_3+H_2O+SO_2=2NaHSO_3+CO_2 ;$$
$$2NaHSO_3+Na_2CO_3=2Na_2SO_3+CO_2+H_2O.$$

Similarly, Sulphur dioxide turns lime water milky due to the formation of insoluble calcium sulphite, which dissolves in excess of the gas (hence the milkiness disappears), forming calcium bisulphite. (cf. CO_2).

$$Ca(OH)_2+SO_2=CaSO_3+H_2O ;$$
$$CaSO_3+H_2O+SO_2=Ca(HSO_3)_2.$$

N. B. Both SO_2 and CO_2 respond this reaction, i.e. both of them turn lime water milky. They can, however, be distinguished by the fact that SO_2 discharges the pink colour of permanganate solution and turns the orange colour of acidified dichromate solution to green. CO_2 has no action on these solutions.

(v) One of the useful reactions of sulphur dioxide is its combination with oxygen in presence of heated catalysts (Pt, V_2O_5, NO etc.) to yield sulphur trioxide $2SO_2+O_2=2SO_3$. This reaction is used in the manufacture of H_2SO_4. Ozone also oxidises sulphur dioxide to trioxide : $3SO_2+O_3=3SO_3$. Sulphur dioxide reacts with chlorine in bright sunlight giving sulphuryl chloride : $SO_2+Cl_2=SO_2Cl_2$.

(vi) An aqueous solution of sulphur dioxide is frequently used in the laboratory as a *reducing agent.* It slowly absorbs oxygen from the air to form sulphuric acid : $2H_2SO_3+O_2=2H_2SO_4$, the reaction is catalysed by the trace of copper or iron salts. Sulphur dioxide reduces halogens to their hydracids, ferric salts to ferrous salts, mercurous nitrate to metallic mercury, hydrogen peroxide to water. It decolourises an acidifie solution of potassium permanganate by reduction, it also reduces acidified solution of porassium dichromate, the colour of the solution changes from orange-yellow to green. Sulphur dioxide liberates iodine from an iodate, but the iodine that is set free is decolorised with excess of sulphur dioxide. It all then reactions, sulphur dioxide is oxidised to sulphuric acid.

(a) $Br_2+SO_2+2H_3O=2HBr+H_2SO_4$.

(b) $Cl_2+SO_2+2H_2O=2HCl+H_2SO_4$.

(c) $2FeCl_3+SO_2+2H_2O=2FeCl_2+2HCl+H_2SO_4$.

(d) $Hg_2(NO_3)_2+SO_2+2H_2O=2Hg+2HNO_3+H_2SO_4$

(e) $H_2O_2+H_2SO_3=H_2O+H_2SO_4$.

(f) $2KMuO_4+5SO_2+2H_2O=K_2SO_4+2MnSO_4+2H_2SO_4$

(g) $K_2Cr_2O_7+3SO_2+H_2SO_4=K_2SO_4+Cr_2(SO_3)_3+H_2O$

(h) $2KIO_3+5SO_2+4H_2O=I_2+2KHSO_4+3H_2SO_4$

(i) $I_2+SO_2+2H_2O=2HI+H_2SO_4$

(vii) Sulphur dioxide in certain conditions can, however. react as an oxidising agent. It oxidises moist hydrogen sulphide to sulphur, and in strongly acid solution ferrous chloride is oxidised to ferric chloride :

(a) $2H_2S + SO_2 = 2H_2O + S$
(b) $4FeCl_2 + SO_2 + 4HCl = 4FeCl_3 + 2H_2O + S$.

At high temperature (1100°C) gaseous sulphur dioxide oxidises carbon to carbon dioxide :

(c) $C + SO_2 = CO_2 + S$.

SO_2 acts as a reductant or an oxidant, as it contains sulphur in an intermediate oxidation state of $+4$.

(viii) When heated to about 150°C in a sealed tube, an aqueous solution of sulphur dioxide deposits sulphur, showing the presence of sulphur in sulphur dioxide.

$$2H_2SO_3 + SO_2 = 2H_2SO_4 + S.$$

(ix) Warmed lead dioxide and sodium peroxide become incandescent when brought into contact with sulphur dioxide, and yield the respective metallic sulphate : $PbO_2 + SO_2 = PbSO_4$; $Na_2O_2 + SO_2 = Na_2SO_4$.

(x) Sulphur dioxide act as a bleaching agent in presence of moisture. Dry SO_2 gas cannot bleach. Organic colouring matter or dyes are bleached by sulphur dioxide. It is believed that sulphur dioxide produces nascent hydrogen from water, which actually bleaches the organic colouring matter : $2H_2O + SO_2 = H_2SO_4 + 2H$. Hence sulphur dioxide bleaches by reduction.

N. B. Both SO_2 and chlorine act as bleacling agents in presence of moisture, but there are differences between their action. (i) SO_2 is a milder bleaching agent than chlorine and hence delicate fabrics, such as wool, silk etc. which are likely to be injured by chlorine, are bleached by sulphur dioxide. (ii) In presence of moisture sulphur dioxide bleaches by reduction whereas chlorine bleaches by oxidation, (iii) substances bleached by SO_2 may sometimes restore their original colours by aerial oxidation, but the bleaching made by chlorine is permanent.

Tests : (i) Sulphur dioxide is recognised easily from its distinctive smell of burning sulphur. (ii) A paper soaked in acidified

$K_2Cr_2O_7$-solution when held in the gas turns green indicating the presence of sulphur dioxide. (iii) It gives a white ppt. with $BaCl_2$-solution, the ppt. is soluble in dil. HCl.

Uses : (i) The main use of sulphur dioxide is in the manufacture of sulphuric acid. (ii) It is also required in the production of bisulphites and metabisulphites used in photography and in paper industry. (iii) It is employed for the bleaching of silk or woollen goods and also as an antichlor. (iv) Liquid SO_2 is a refrigerant. (v) Sulphur dioxide is sometimes used for disinfection.

29·15. Volumetric composition of sulpher dioxide :

The composition of sulphur dioxide is determined by burning a piece of sulphur in an enclosed volume of oxygen. The arrange ment is shown in Fig 29·9. The apparatus consists of U-shapped eudiomter tube, one end of which ends in a stoppered globe. Through the stopper enter two copper wires, one of which ends in a small spoon. The spoon is connected to the other wire by a thin platinum spiral. A small amount of pure sulphur is taken on the spoon and the globe and part of the endiometer tube is filled with oxygen over mercury under atmospheric pressure. A current is passed through the two wires and the platinum spiral is heated enough to ignite sulphur in the spoon, which is transformed into sulphur dioxide. After the burning is complete, the apparatus is cooled and the volume of the gas is noted. It is found that the volume of the gas is not changed at all. That is, the volume of sulphur dioxide produced is the same as that of oxygen used up. *Sulphur dioxide contains its own volume of oxygen.* Hence,

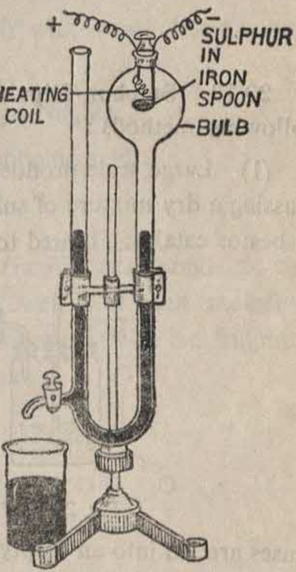


Fig. 29·9. Volumetric composition of sulphur dioxide

x volumes of sulpher dioxide contains x volume of oxygen. or, by Avogadro's hypothesis n moleculs of sulpher dioxide contain n molecules of oxygen

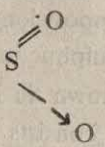
or, 1 molecule of sulpher dioxide contains 1 molecule of oxygen

or, 1 molecule of sulpher dioxide contains 2 atom of oxygen

Therefore the molecular formula of sulpher dioxide is S_xO_2. The vapour density of the gas has been found to be 32, i.e. its moleculer weight $= 32 \times 2 = 64$.

$\therefore\ 32 \times x + 32 = 64$, or $x = 1$.

Hence the molecular formula of sulphur dioxide is SO_2. Sulphur dioxide is a polar molecule. It cannot have a linear symmetrical structure. The structure of molecule is



29·16. Sulphur Trioxide, SO_3—This oxide is prepared by the following methods :

(1) Large scale production of sulphur trioxide is carried out by passing a dry mixture of sulphur dioxide and oxygen over platinifed asbestos catalyst, heated to 450°C in a glass tube. The outcoming gases are led into an empty receiver cooled in a freezing mixture. Sulphur trioxide condences there as transparent crystals (Fig 29.10).

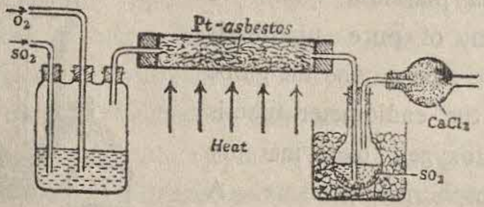


Fig. 29·10. Preparation of sulphur trioxide

$$2SO_2 + O_2 = 2SO_3\ ;\quad \Delta H = -44{\cdot}4 \text{ K cal.}$$

(2) Sulphur trioxide is also prepared by heating anlydrous ferric sulphate or sodium pyrosulphate or by distilling concentrated sulphuric acid with an excess of phosphorus pentoxide :

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$$
$$Na_2S_2O_7 = Na_2SO_4 + SO_3$$
$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3$$

Properties : (1) Sulphur trioxide occurs as colourless crystals. It exists in two allotropic modification : α—sulphur trioxide, colourless needles, m. pt. 17°C, b. pt. 44·5°C, and β—sulphur trioxide, an asbestos-like solid, which sublimes at 50°C. The α—form reverts to the β—form on keeping in presence of moisture.

(ii) Sulphur trioxide fumes in moist air, as the vapour combines with water to form droplets of sulphuric acid, hence it is the anhydride of sulphuric acid. It reacts violently with water to form sulphuric acid and pyrosulphuric acid, also called *oleum.*

$$SO_3+H_2O=H_2SO_4\ ;\quad 2SO_3+H_2O=H_2S_2O_7$$

Technically, concentrated sulphuric acid (98%) is employed as a solvent for sulphur trioxide to produce *oleum* or *fuming* sulphuric acid.

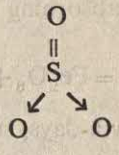
(iii) Sulphur trioxide combines directly with some basic oxides and form sulphates :

$$BaO+SO_3=BaSO_4\quad Na_2O+SO_3=Na_2SO_4.$$

With hydrochloric acid its gives chlorosulphonic acid :

$$SO_3+HCl=Cl.SO_2OH.$$

The density of the vapour of sulphur trioxide corresponds to the moleculer formula SO_3. It is a non-polar molecule, each molecule having a planar, equilateral triangle arrangment with the sulphur atom at the centre. The molecular structure is



29·17. Sulphurous Acid :

Sulphurous acid is merely a solution of SO_2 in water and so it is prepared by dissolving the gas in water : $SO_2+H_2O\rightleftharpoons H_2SO_3$. As already stated, sulphurous acid is not available in the pure state and it exists only in solution. Its salts are, however, available in the pure state.

It is a dibasic acid and reacts with alkalis forming two types of salts—bisulphites and sulphites. These salts are usually prepared by the action of sulphur dioxide on alkalis :

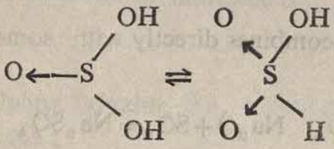
$$H_2SO_3 + NaOH = NaHSO_3 + H_2O$$
$$NaHSO_3 + NaOH = Na_2SO_3 + H_2O$$

Sodium sulphite when heated yields sodium sulphide and sulphate :

$$4Na_2SO_3 = Na_2S + 3Na_2SO_4.$$

Sulphites are decomposed by dilute acids with the evolution of sulphur dioxide.

Sulphurous acid, being a solution of sulphur dioxide, has the properties of the latter. It is a reducing agent like sulphur dioxide and has also bleaching properties. The structural formula of sulphurous acid is represented as :



29·18. Sulphuric acid, oil of vitriol, H_2SO_4

Free sulphuric acid does not occur in nature but in the combined state it occurs as sulphates in many minerals, such as *gypsum*, $CaSO_4$, $2H_2O$, *kieserite*, $MaSO_4$, H_2O , Barytes, $BaSO_4$ etc. In old days sulphuric acid used to be prepared by distilling green vitriol and absorbing the vapours in water, and was called "*oil of vitriol*".

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3 , \quad SO_3 + H_2O = H_2SO_4$$

But now-a-days, sulphuric acid is always produced from SO_2. Its demand is so high that it is a basic chemical industry in every country and it is always prepared in manufacturing scale.

29·19. Manufacture of sulphuric acid :

Sulphuric acid is manufactured by two processes from the sulphur dioxide obtained by roasting sulphur or metallic sulphides in air :

(i) The Lead Chamber Proces ,

(ii) The Contact Process.

The first process, which is cheaper is used to meet the demand of dilute acid for ordinary purposes, where as the second process is employed when very pure and concentrated acid is required. In both the processes, SO_2 is first oxidised to SO_3 by oxygen of the air with the help of a suitable catalyst. Sulphur trioxide then takes up water forming sulphuric acid.

29·20. The Lead chamber Process :

This is the oldest process for the manufacture of sulphuric acid. The principle of the chamber process is the oxidation of most sulphur dioxide by atmospheric oxygen in the presence of oxides of nitrogen which act as a homogeneous catalyst. The process is worked as follows :—

(1) Sulphur dioxide is produced by burning sulphur or from the roasting of sulphide ores (e.g., iron pyrites FeS_2 and zinc blende, ZnS) in *burners* A. (Fig 29·11)

$$S+O_2=SO_2\ ;\quad 4FeS_2+11O_2=2Fe_2O_3+8SO_2\ ;$$
$$2ZnS+3O_2=2ZnO+2SO_2.$$

(2) The gases leaving the burners, contain about 8 percent sulphur dioxide, 10 percent oxygen and the rest nitrogen ; they pass through *nitre-ovens*, where oxides of nitrogen are supplied by distilling a mixture of sodium nitrate and strong sulphuric acid from *nitre pots* (B). In modern plants oxides of nitrogen are supplied by catalytic oxidation of ammonia.

(3) The gases are then passed through a dust catcher (C). containing baffle-walls, where suspended particles carried from the burners settle down.

(4) The hot gas mixture at about 300-400°C, then enters the bottom of a tower (D), called *Glover tower*. This tower is packed with *acid-proof* bricks. From the top of this tower run down simultaneously two separate streams of H_2SO_4 (65%) and nitrosylsulphuric acid, ($NOHSO_4$). Both these acids are available from this very process. The oxidation of SO_2 begins from this tower. Several functions are perfomed in this tower : (i) the reactant gas

mixture is cooled to about 50°C ; (ii) the falling 65% H_2SO_4 is concentrated by evaporation to 78% which collects at the bottom ; (iii) the falling nitro-acid is decomposed to H_2SO_4 and the oxides of nitrogen are set free to be used again ; (iv) some quantity of H_2SO_4 also is formed from SO_2 in this tower. All the sulphuric acid accumulate in a tank below. The acid is 78%.

$$2NOHSO_4 + H_2O = 2H_2SO_4 + NO + NO_2$$
$$2SO_2 + O_2 + 2H_3O = 2H_2SO_4$$

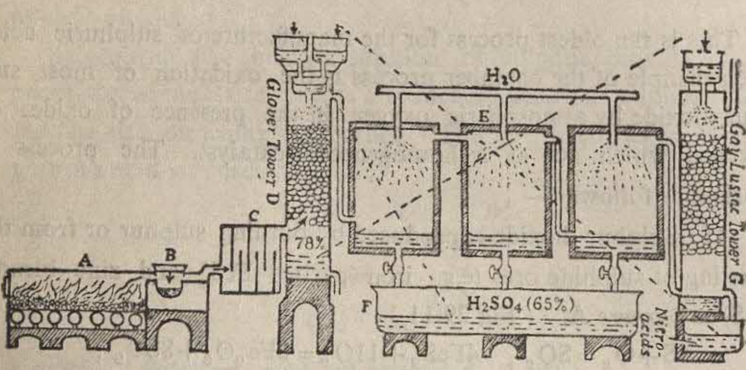


Fig. 29·11. Sulphuric acid by the Lead Chamber Process

A—Burners ; B—nitre-pot ; C—dust catcher ; D—Glover tower E—Lead Chamber, F—storage of 65% acid, G—Gay-Lussae tower.

(5) Coming out from the top of the Glover tower, the gases pass successively through three or four very large lead-lined wooden chambers (E). The temperature is maintained at 30° ~ 40°C. Water is sprayed into the chambers from the top. Here in these lead chambers, the bulk of the acid is formed and hence the name of the process. The formation of the acid with the help of the catalyst is explained in different ways. One possible explanation is the formation of nitrososulphuric acid first which then hydrolyses into the acid.

$$2SO_2 + NO + NO_2 + O_2 + H_2O = 2SO_2(OH)ONO$$
(nitroso sulphuric acid)

$$2SO_2(OH)ONO + H_2O = 2H_2SO_4 + NO + NO_2$$

An alternative mechanism suggests that nitrogen dioxide oxidises sulphur dioxide to sulphur trioxide, which is then absorbed in water forming sulphuric acid ; the resulting nitric oxide is again converted to nitrogen dioxide by oxidation with oxygen, which reacts again. So the formation of the intermediate compound NO_2 has been suggested in the explanation.

The acid formed in these chambers attains a strength of 65% and is collected at the bottom in a tank. The whole of this chamber acid is pumped to the top of the Glover tower. On running down the tower, the acid is concentrated to 78% strength.

(6) Any unreacted SO_2, air and, more important, the oxides of nitrogen coming out of the lead chambers enter into the bottom of a tower called *GAY-LUSSAC TOWER.* This tower is packed with hard coke and conc. H_2SO_4 (78%) is run down from the top. This acid is a small part of which collects at the bottom of the Glover tower. The purpose of this tower is to recover the valuable catalyst, oxides of nitrogen for recycling. Sulphuric acid absorbs the oxides of nitrogen and forms nitrosyl sulphuric acid, $NOHSO_4$.

$$2H_2SO_4 + NO + NO_2 = 2NOHSO_4 + H_2O$$

The nitrosyl sulphuric acid is wholly pumped to the top of the Glover tower. The oxides of nitrogen are set free there. Thus the same catalyst is utilised over and over again. Some replenishments are necessary due to unavoidable losses. This is how sulphuric acid is manufactured in the lead chamber process.

Concentration of chamber acid :—

The 78% H_2SO_4 obtained from the Lead Chamber process is often concentrated further in the cascade process. The acid is allowed to flow down a series of silica or ferrosilicon basins arranged one below another in a sloping floor (Fig. 29.12). The basins are heated from below by hot gases of coke-fire. Acid is heated and concentrated and steam escapes by an outlet at the top. The acid concentration may thus be raised to 95%. This acid is then heated in cast iron pans by direct fire and 98% H_2SO_4 can be obtained.

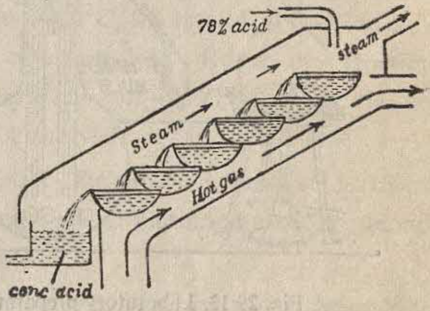


Fig. 29·12. Concentration of H_2SO_4

Purification of chamber acid. The impurities likely to be present in commercial sulphuric acid are lead sulphate, arsenious oxide, and nitrous acid. The metals are removed by diluting the actd to 60 percent, when lead sulphate, being insoluble in dilute acid, separates. The diluted acid is then treated with hydrogen sulphide in lead tower,—the insoluble sulphides of lead and arsenic are precipipated and filtered off. Nitrous acid is then removed by heating the acid with a little ammonium sulphate :

$$2HNO_2 + (NH_4)_2SO_4 = H_2SO_4 + 2NH_4NO_2$$
$$NH_4NO_2 = N_2 + 2H_2O.$$

29·21 Laboratory illustration of chamber process :

The principle of the lead chamber process can be illustrated in the laboratory. A large dry flask of about 5 litre capacitry is closed by means of a cork through which are inserted four long inlet tubes, almost reaching the bottom and a short exit tube for gases.

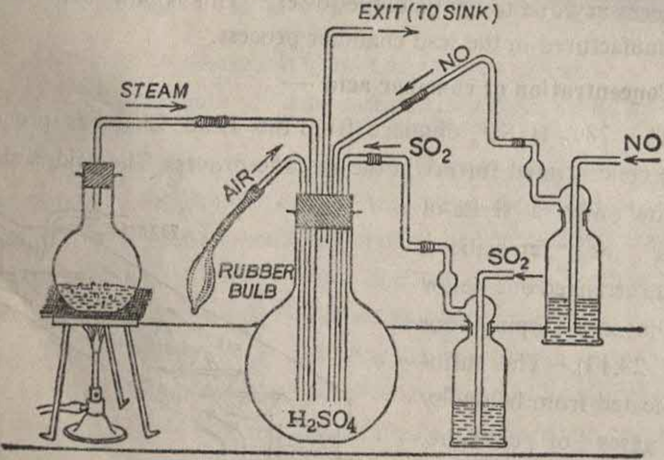


Fig. 29·13. Laboratory preparation of sulphuric acid.

Through the four inlet tubes are introduced (a) nitric oxide (prepared from copper and 1 : 1 HNO_3), (b) Sulphur dioxide (prepared by heating copper turnings with conc. H_2SO_4), (c) Steam and (d) oxygen or air (pumped by hand bellows). At first a stream of oxygen is passed into the flask, then nitric oxide and then sulphur dioxide and finally steam are admitted. The supply of air must be plentiful and the SO_2 should be much in excess of nitric oxide. The reactions similar to those in the lead chambers occur with the formation of dilute sulphuric acid, which collects at the bottom of the flask (Fig 29·13).

29·22. The Contact Process :

The essentral features of the contact process are the catalytic oxidation of sulphur dioxide to sulphur trioxide by atmospherie oxygen, followed by absorption of the latter in concentrated sulphuric acid. The resultant fuming sulphuric acid is diluted with water to yield 100 percent acid :

$$2SO_2 + O_2 = 2SO_3$$
$$SO_3 + H_2SO_4 = H_2S_2O_7 \text{ (oleum)}$$
$$H_2S_2O_7 + H_2O = 2H_2SO_4 \text{ (100\%)}.$$

The raw materials are the same as those in the chamber process —sulphur, air and water.

Theoretical considerations : (a) The formation of SO_3 by the oxidation of SO_2 with oxygen is an exothermic reversible reaction :

$$2SO_2 + O_2 \rightleftharpoons 2SO_3,\ \Delta H = -\ 45000 \text{ cal.}$$

It follows from Le chateliar principle that the reaction is favoured at low temperature. But below 400°C, the rate of formation of SO_3 is too slow even in presence of a catalyst. Hence the reaction is carried out at an *optimum temperature* of 450°C, at which the speed of reaction is not too slow, nor the yield of SO_3 is too low.

(b) To speed up the reaction, the use of a catalyst is essential. In this process, the catalyst employed is platinised asbestos, vanadium pentonide or platinised silicagel.

platinised asbestos is made by gently heating asbestos moistened with a solution of ammonium platinichloride, $(NH_4)_2PtCl_6$. The platinum salt decomposes and deposits a residue of fineely divided platinum on asbestos : $(NH_4)_2PtCl_6 = 2NH_3 + 2HCl + 2Cl_2 + Pt$.

(c) The reaction is accompanied with a decrease in volume.

Hence, according to Le chatelier principle, the reaction will be favoured at high pressures. But even at ordinary pressure, nearly 98% of SO_2 is oxidised, so it is not necessary to employ high pressure here.

(d) The equilibrium constant for the reaction $2SO_2+O_2 \rightleftharpoons 2SO_3$ is given by : $K=\dfrac{p^2_{SO_3}}{p^2_{SO_2} \times p_{O_2}}$. At any given temperature, K remains constant. From the above equation it is clear that if the partial pressure of oxygen ($^{P}O_2$) is increased, the partial pressure of SO_3 ($^{p}SO_3$) and hence its concentration would increase. This is why excess oxygen (or air) is always used in the process.

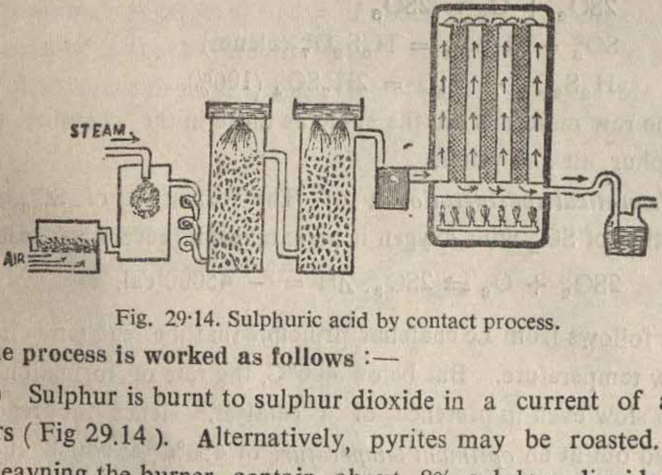


Fig. 29·14. Sulphuric acid by contact process.

The process is worked as follows :—

(1) Sulphur is burnt to sulphur dioxide in a current of air in burners (Fig 29.14). Alternatively, pyrites may be roasted. The gases leavning the burner contain about 8% sulphur dioxide, 10% oxygen and the rest nitrogen. There are also present impurities like dust particles, arsenious oxide, sulphuric acid mist etc. in the burner gases which poison the catalyst, especially where platinised asbestos catalyst is used. Hence they are removed before the gases enter the contact chamber.

(2) The burner gases are carefully cleaned by passing in succession through :

(a) *a dust chamber*—in which steam is injected to remove arsenious oxide, dust, sulphuric acid mist etc.

(b) Water cooled *lead coils* to reduce the temperature of the gas,

(c) a wash tower—packed with flint balls, down which water is sprayed to wash out the impurities and finally, (d) a drying tower-a lead tower packed with coke over which 98 percent cone. H_2SO_4 trickles down to arrest acid mist and to dry the gases.

(3) The dry and purified gases are examined agains a beam of light through an inspection window to appear perfectly transparent, i.e., the gas mixture should be *optically clear.*

(4) The purified gases are then led into the catalyst chamber, called the *converter*, through a heat exchanger (not shown in the figure), where they are pre-heated by the hot resultant gases (SO_3 and air) coming out of the catalyst chamber. The *converter* is an iron cylinder fitted inside with vertical iron tubes packed with the catalyst (platinised asbestos or vanadium pentoxide). The hot incoming gases enter the chamber, circulate round the hot tubes and then pass down them when sulphur dioxide is rapidly converted into sulphur trioxide in contact with the catalyst. The heat of reaction is sufficient to maintain the optimum temperature of 450°C necessary for the reaction—no external heat is needed after once the reaction has started.

(5) Nearly 98% of the sulphur dioxide is oxidised to sulphur trioxide. The gases leaving the converter at the bottom consist principally of sulphur trioxide and nitrogen.

It then enters into the heat exchanges, where it parts with its heat. Comparatively cold gas is then passed into a cast iron tank containing 98 *percent concentrated sulphuric acid* in which sulphur trioxide is completely absorbed forming oleum or fuming sulphuric acid : $SO_3 + H_2SO_4 = H_2S_2O_7$

The latter, on dilution with water, yidds the concentrated 100 percent sulphuric acid : $H_2S_2O_7 + H_2O = 2H_2SO_4$

Sulphur trioxide cannot be directly absorbed by water since it will form fine mist of sulphuric acid which cannot be condensed.

29·23. Comparison between Chamber process and Contact process.

Chamber process	Contact process
1. Acid obtained is dilute (65 to 70%), may be concentrated by special method.	1. Directly produces 100% sulphuric acid and obeum. No further concentration is necessary.
2. Chamber acid is less pure.	2. Acid obtained is pure.
3. The operation of the process is not so easy as the contact process.	3. The operation of the process is easier.
4. The weak chamber acid is suitable for use in the manufacture of salt cake, superphosphate, ammonium sulphate, etc.	4. The concentrated contact acid is used in the refining of petroleum, in synthetic dye and drug industries and in explosives.

29·24. Properties of sulphuric acid :

(1) Pure sulphuric acid is a heavy colourless oily liquid (sp. gr. 1·838 at 15°C). The acid freezes at 10·4°C, and boils at 338°C (with decomposition) giving out dense white fumes of SO_3 and water and forming a constant boiling mixture of 98·3 per cent acid. It is a highly corrosive liquid and must be handled with care.

(ii) The pure acid is almost non-conductor of electricity, but in an aqueons solution it is a good conductor.

(iii) The pure acid has a strong affinity for water. It dissolves in water with the evolution of large amount of heat :

$$H_2SO_4 + Aq = H_2SO_4, Aq. \quad \Delta H = -216900 \text{ cal.}$$

From the aquons solution, the hydrates H_2SO_4, H_2O ; H_2SO_4, $2H_2O$; and H_2SO_4, $4H_2O$ can be crystallised out. When dilution required, *the concentrated acid should always be added to water and never the reverse.* It water be added to the strong acid, the first few drops of water may change into steam suddenly causing the acid to spurt in all directions. Because of this marked affinity for water, conc. H_2SO_4 is very much used as a *dehydrating agent,* to dry gases such as oxygen, nitrogen, sulphur dioxide, chlorine etc., on which it does not react chemically. It is also used in desiccator.

(iv) Concentrated sulphuric acid is even capable of removing the elements of water from some compounds. Thus sugar and starch are charred by the acid with separation of carbon.

$$\underset{\text{(Sucrose)}}{C_{12}H_{22}O_{11}} \xrightarrow[-11H_2O]{H_2SO_4} 12C$$

$$\underset{\text{(glucose)}}{C_6H_{12}O_6} \xrightarrow[-6H_2O]{H_2SO_4} 6C$$

Oxalic acid, formic acid, alcohol are similarly dehydrated thus :

Formic acid : $HCOOH - H_2O = CO.$

Oxalic acid : $(COOH)_2 - H_2O = CO + CO_2$

Ethyl alcohol : $C_2H_5OH - H_2O = C_2H_4$

(v) In aqueous solution sulphuric acid is a strong dibasic acid and produces both acid and normal salts, such as $NaHSO_4$ (sodium bisulphate) and Na_2SO_4 (Sodium sulphate).

In *dilute solution*, sulphuric acid ionises as

$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}.$

But in very *concentrated solution,* the ionisation takes places as : $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$. This explains the formation of perdisulphuric acid at the anode during the electrolysis of concentrated sulphuric acid solution. At the anode : $HSO_4^- - e = HSO_4$; $2HSO_4 = H_2S_2O_8$ (perdisulphuric acid).

Dilute sulphuric acid usually reacts with metals standing above hydrogen in the electrochemical series liberating hydrogen and a salt of the metal.

$$H_2SO_4 + Fe = FeSO_4 + H_2 \ ; \ H_2SO_4 + Zn = ZnSO_4 + H_2.$$

At ordinary temperatures it neutralises alkalis and liberates carbondioxide from carbonates.

(vi) Hot concentrated sulphuric acid behaves as an oxidising agent, and dissolves many metals like Zinc, lead, silver, copper, standing both above and below hydrogen in the electrochemical series, producing sulphur dioxide, water and salt of the metal :

$Pb+2H_2SO_4=PbSO_4+SO_2+2H_2O$;

$Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O$.

Hot concentrated sulphuric acid oxidises carbon, sulphur, phosphorus, hydrogen, hydrobromic and hydroiodic acids. In all these reaction, sulphuric acid is reduced to SO_2.

$$C+2H_2SO_4=CO_2+2SO_2+2H_2O$$
$$S+2H_2SO_4=3SO_2+2H_2O$$
$$P_4+6H_2SO_4=4H_3PO_3+6SO_2$$
$$H_2+H_2SO_4=SO_2+2H_2O$$
$$2HI+H_2SO_4=I_2+SO_2+2H_2O$$
$$2HBr+H_2SO_4=Br_2+SO_2+2H_2O$$

(vii) At higher temperatures, conc. sulphuric acid being relatively less volatile displaces the stronger and more volatile nitric and hydrochloric acids, from their salts :

$NaCl+H_2SO_4 \rightleftharpoons NaHSO_4+HCl$;

$NaNO_3+H_2SO_4 \rightleftharpoons NaHSO_4+HNO_3$

(viii) Sulphuric acid decomposes into sulphur dioxide, water and oxygen when dropped on red hot pumic stone taken in a flask : $2H_2SO_4=2H_2O+2SO_2+O_2$. The gases are allowed to pass in succession through two U-tubes, one placed in cold water and the other in a freezing mixture. The liquid collceted in the first U-tube, is recognised to be water by its action on anhydrous copper sulphate (turns blue), this shows the presence of hydrogen in sulphuric acid. In the second U-tube sulphur dioxide condenses to a liquid and the gas passes out is shown to be oxygen as it rekindles a glowing piece of wood. when an aqueons solution of the liquid collceted in the second U-tube is heated to 150°C in a sealed tube, sulphur separates. These experiments show that *sulphuric acid contanis hydrogen, oxygen and sulphur.*

(ix) Sulphuric acid frequently employed as a *sulphonating agent* for organic compounds, In such reaction, hydrogen in aromatic molecules, say benzene, is substituted by sulphonic-radial (SO_3H) :

$$C_6H_6+H_2SO_4=\underset{\text{(benzene sulphonic acid)}}{C_6H_5SO_3H}+H_2O.$$

29·25. Uses of sulphuric acid :

Sulphuric acid has extensive uses in various industries and the economy of advanced countries pimarily depends on the large scale production of H_2SO_4. It is used (i) in the manufacture of hydrochloric and nitric acids, paints, pigments, etc ; (ii) in the preparation of alum, fertilisers such as superphosphate, ammonium sulphate ; (iii) in rayon industry and in the refining of petroleum ; (iv) in the manufacture of explosives like TNT, nitrocelluloses, picric acid etc ; (v) to prepare sulphonated aromatic compounds from which various dyes, drugs etc. are produced ; (xi) in lead accumulators ; (vii) for steel-pickling and cleaning iron sheets before galvanizing ; (viii) for refining petroleum and (ix) as a laboratory reagent.

Test for sulphuric acid and sulphates :

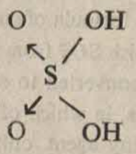
(i) When barium chloride solution is added to a solution of sulphuric acid or a sulphate acidified with hydrochloric acid, a heavy white precipitate is formed indicating the presence of sulphate (SO_4^{--}).

$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl.$$

The precipitate is insoluble in HCl or HNO_3.

(ii) On heating with copper turnings, H_2SO_4 evolves SO_2 which is recognised by its smell of burning sulphur.

The molecular structure of sulphuric acid is represented as



Exercise—29

1. What are the allotropic modifications of sulphur ? Give their properties and uses. How would you prove that the different allotropes are the same element, sulphur ?

2, Explain how β-sulphur is prepared from α-sulphur. Describe what you would observe if α-sulphur is continuously heated to high temperature.

3, Mention the principal sources of sulphur. Describe briefly the process employed to obtain sulphur from the underground deposit.

4. (a) Starting with roll sulphur show how would you prepare (i) sulphur dioxide, (ii) sulphur trioxide, (iii) hydrogen sulphide, (iv) sodium thioulphate, and (v) sulphuric acid.

(b) Give examples to illustrate the different oxidation states of sulphur.

(c) How does sulphur react with (i) chlorine, (ii) caustic soda, (iii) nitric acid, (iv) sulphuric acid, (v) iron, (vi) sodium sulphide, (vii) lime

5. Describe with a neat sketch of the apparaturs, how hydrogen sulphide is prepared in the laboratary, How is the gas purified and dried ? Why nitric acid is not used in the preparation of this gas ?

6. How would you prove that

(a) hydrogen sulphide contains hydrogen and sulphur and its molecular formula is H_2S ?

(b) hydrogen sulphide is a reducing agent and a very weak dibasic acid ?

7. Describe the reaction of hydrogen sulphide with (a) oxygen, (b) Br_2-water (c) ferric chloride solution, (d) cupric chloride solution , (e) potassium Permanganate solution, (f) lead acetate solution, (g) sulphur dioxide, (h) dilute nitric acid, (i) iodine suspension in water.

8. Discuss the use of H_2S as a reagent for chemical analysis. How is the gas prepared for this purpose ?

9. (a) How will you prepare pure and dry sulphur dioxide ? Illustrate with equation its behaviour as a reducing agent, as an oxidising agent and as an acidic oxide.

(b) Compare the bleaching properties of sulphur dioxide and chlorine.

10, How would sulphur dioxide react with (a) H_2S, (b) $KMnO_4$ solution, (c) $K_2Cr_2O_7$ solution, (d) lime water, (e) chlorine, (f) a mixture of nitrogen dioxide and water vapour, (g) lead dioxide (h) caustic potash solution ?

11. (a) Prove that the molecular formula of sulphur dioxide is SO_2

(b) How would you distinguish $SO_3^=$ from CO_2 by chemical methods ?

(c) How is sulphur dioxide converted to sulphur trioxide ?

(d) Explain with illustrations, in which of the following substances can sulphur act as a reducing agent only, in which only as an oxidising agent and in which as both : H_2S, S, SO_2 and H_2SO_4.

(e) discuss the reducing properties of sulphurous acid.

12. Discuss the physico-chemical principles involved in the preparation of sulphuric acid by the contact process. Give a very brief outline of the process.

13. (a) Since SO_3 is the analydride of sulphuric acid, why is it not prepared by directly dissolving SO_3 in water ?

(b) How would you prove that sulphuric acid contains hydrogen, sulphur and oxygen ?

14. (a) Discribe experiments to show that sulphuric acid acts as (i) an acid, (ii) a dehydrating agent, (iii) an oxidising agent.

(b) Describe the action of 'sulphuric acid upon: (i) oxalic acid, (ii) potassium bromide, (iii) common salt, (iv) chile saltpetre, (v) sugar, (vi) sulphur, (vii) a mixture of calcium fluoride and sand (viii) copper. Give equations.

15. (a) How would you distinguish between a soluble sulphate and a sulphide.

(b) Explain why: (i) the boiling point of water is much higher than that of H_2S, (ii) H_2S solution becomes turbid on keeping, (iii) violet vaporus are evolved on heating KI with concentrated H_2SO_4 ?

16. How is sulphuric acid manufactured by the lead chamber process? How would you imitate the process in the laboratory? How the acid is concentrated? outline the principal uses of the acid.

17. Balance the following equation with the help of oxidation number changes:

(i) $FeCl_3 + H_2S \rightarrow FeCl_2 + S + HCl$

(ii) $HNO_3 + H_2S \rightarrow NO_2 + S + H_2O$

(iii) $Br_2 + SO_2 + H_2O \rightarrow HBr + H_2SO_4$

CHAPTER XXX

HALOGENS

The halogens form a closely related family of four elements, *Fluorine*, *Chlorine*, *Bromine* and *Iodine*, remarkable for their similarity of chemical behaviour and for the gradation of their physical properties with increasing atomic weight. These are all non-metallic elements belonging to the same group of the Periodic Table. The word "halogen" means "sea-salt producer". The name was applied to this group as the last three elements of the family are contained in sea water, and their sodium salts resemble the sea-salt, sodium chloride. Due to their highly reactive character, none of the halogens are found in the free state in nature.

FLUORINE

Formula F_2, atomic weight 19·00, atomic number 9, electronic configuration $1s^2 2s^2 2p^5$.

30·1. History and occurrence :

Fluorine, the first member of the halogen family, has been known in the form of fluorspar (calcium fluoride) since early days. The element, however, was first isolated by Moissan in 1886.

Fluorine is too active to occur free in nature, but in combination it occurs in nature quite abundantly. The most importont minerals of fluorine are *fluorspar*, CaF_2, *Cryolite*, 3NaF, AlF_3 and *fluorapatite*, CaF_2, $3Ca_3(PO_4)_2$. The enamel of teeth contains 0·3 per cent. of flourine.

30·2. Preparation :

Hydrofluoric acid and several compounds of fluorine were known long before the element was isolated. All attempts to liberate the free fluorine by use of oxidising agents failed, because the element itself is the most vigorous oxidising agent, and reacts with almost every substance. As the hydrofluoric acid resembled hydrochloric acid in many properties, attempts were made by Devy, Gore and others to isolate the element by the electrolysis of an aqueous solution of hydrofluoric acid. But their attempts were uniformly fruitless due to the following reasons :

(i) The products of electrolysis were found to consist not of hydrogen and fluorine but of hydrogen and ozonised oxygen, since the liberated fluorine attacked water :

$$2H_2O+2F_2=4HF+O_2 \ ; \ 3H_2O+3F_2=6HF+O_3.$$

Anhydrous hydrofluoric acid, on the other hand, was found to be non-conductor of electric current.

(ii) It attacked all the materials of the apparatus in which it was tried to be prepared. It was difficult to obtain an electrolytic vessel of fluorine-resistant material.

(iii) Hydrofluoric acid is highly volatile (b. pt. 19·5°C), want of a suitable refrigerant was also partially responsible for the failure of the earlier attempts to isolate fluorine.

Moissan got rid of these difficulties and was successful to isolate fluorine in 1886. The method employed by Moissau to isolate fluorine is briefly outlined as follows :

Moissan's method of preparation : The electrolysis was carried out in a U-tube (Fig 30·1) made of platinum-irridium alloy (which

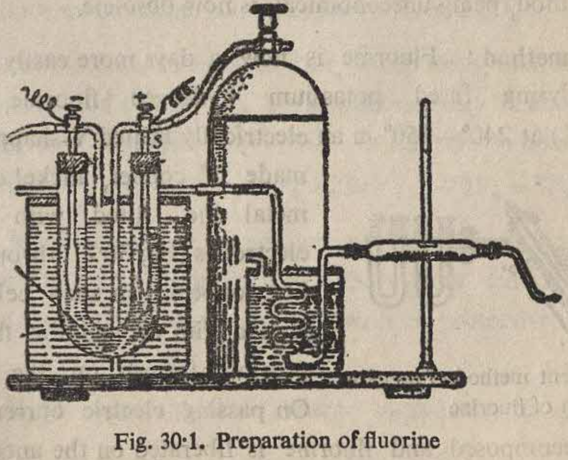


Fig. 30·1. Preparation of fluorine

could resist the action of fluorine), and fitted with calcium fluoride stoppers through which electrodes made of the same alloy and somewhat thickened at the ends were introduced. The U-tube was provided with two side tubes for leading out the gases liberated at the electrodes. The electrolyte was *anhydrous liquid hydrogen fluoride* containing *potassium hydrogen fluoride* (*20%*) to render it a conductor of electric current. The apparatus was immersed in a bath of *boiling methyl chloride*, b.p. −23°C, constantly renewed in order to prevent the vaporisation of hydrogen fluoride, and a potential was applied. During electrolysis hydrogen was evolved at the cathode and fluorine at the anode. Fluorine thus liberated, came out of the side tube and was first led through a spiral tube of platinum cooled to −23°C, by being kept immersed in methyle chloride, to condense the accompanysing vapours of hydrogen fluoride. The gas was then led through a platinum tube packed with fused sodium fluoride to remove the last trace of HF vapours. Fluorine was then collected in a platinum vessel by the upward displacement of air.

$$KHF_2 = KF + HF \;;\; KF \rightleftharpoons K^+ + F^-$$

At anode, $F^- - e = F \;;\; F + F = F_2$

At cathode, $K^+ + e = K \;;\; 2HF + 2K = 2KF + H_2$.

Potassium fluoride, KF, thus formed again under goes electrolysis, HF acid acting as an ionising solvent only.

The method, being uneconomical, is now obsolete.

Recent method : Fluorine is now a days more easily prepared by electrolysing fused potassium hydrogen fluoride, KHF_2 (m.p. 239°C) at 240°—250° in an electrically heated V-shapped vessel made of copper, nickel or monel metal and fitted with graphite electrodes (Fig 30·2) through bakelite stoppers. In such cell, a protective filim of metallic fluoride is possibly formed on the surface. On passing electric current, fused KHF_2 is decomposed and fluorine is liberated on the anode. The gas is led through several copper U-tubes containing dry sodium

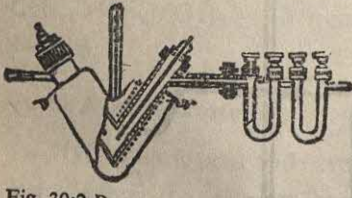


Fig. 30·2 Recent method of preparation of fluorine fluoride, to free it from HF vapours,and is then collected by the displacement of air in the usual way. Hydrogen is evolved from the cathode. Fluorine is now safely compressed and transported in steel, nickel or monel metal cylinders.

30·3. Properties :

(i) Fluorine is a pale, greenish-yellow, poisonous gas with a strong pungent odour. It condenses to a yellow liquid of b.p. $-187°C$, and on further cooling to a pale yellow solid melting at $-233°C$. Fluorine has little action on glass below 100°C and hence can be collected in dry glass vessels.

(ii) Fluorine is the most electronegative and hence most reactive element known. It unites with nearly all elements except nitrogen and the inert gases. The important reactions of fluorine are given below.

(a) Fluorine has a great affinity for hydrogen with which it combines with explosive violence even at a low temperature and in the dark.

(b) It does not react directly with oxygen and nitrogen. At low temperature and pressure and under the influence of electrical discharge, fluorine combines with oxygen to form F_2O_2.

Other non-metals such as sulphur, phosphorus, charcoal, bromine, iodine, boron and silicon, etc., burn spontaneously in the gas yielding their fluorides. Chlorine combines with fluorine on heating.

$$C+2F_2=CF_4 \;;\; Br_2+F_2=2BrF \;;\; S+3F_2=SF_6.$$

(c) Most metals, e.g., sodium, potassium, calcium, magnesium and antimony catch fire in fluorine, others react with incandescence on heating. Copper becomes coated with a protective layer of its fluoride.

(d) With water fluorine reacts vigorously to give ozonised oxygen :

$$2F_2+2H_2O=4HF+O_2 \;;\; 3F_2+3H_2O=6HF+O_3.$$

(e) Fluorine reacts with dilute alkalis liberating fluorine monoxide, whereas with concentrated alkalis, oxygen is produced :

$$\underset{\text{(dil)}}{2NaOH}+2F_2=F_2O+2NaF+H_2O$$

$$\underset{\text{(conc.)}}{4NaOH}+2F_2=O_2+4NaF+2H_2O$$

(f) Fluorine is an intense oxidising agent. Thus it oxidises potassium chlorate to perchlorate and potassium sulphate to persulphate. It also liberates the halogens from their hydracids and salts :

$$2HCl+F_2=2HF+Cl_2\ ;\ \ 2KBr+F_2=2KF+Br_2.$$

(g) Many organic substances, like ether, alcohol, turpentine, etc., take fire in the gas spontaneously and are completely decomposed.

CHLORINE

Formula Cl_2, Atomic number 17, Atomic weight 35·46, Electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^5$.

30·4. History and Occurrence :—Chlorine was discovered by Scheele in 1774 by heating hydrochloric acid with manganese dioxide, but it was conclusively proved to be an element by Davy in 1810, who proposed the name chlorine for this gas because of its greenish yellow colour.

Chlorine does not occur in the free state. It is mostly present in the form of sodium chloride (NaCl) or common salt in seawater and in some rock-salt mines. It also occurs abundantly in minerals like *sylvine*, KCl, and *carnallite*, $KCl,MgCl_2,6H_2O$ in the Stassfurt salt deposits. It also occurs as horn-silver, AgCl.

30·5. Preparation : *Laboratory method*—chlorine is usually prepared in the laboratory by oxidising concentrated hydrochloric acid by (i) pyrolusite (the mineral form of manganese dioxide, MnO_2) or

(ii) potassium permanganate, $KMnO_4$.

(i) powdered manganese dioxide (pyrolusite) is taken in a round-bottomed flask fitted with a thistle funnel and a delivery tube

(Fig 30.3). Concentrated hydrochloric acid is poured down the funnel in quantity, so that it covers MnO_2 and the end of the funnel dips into the acid. On heating, the reaction starts and chlorine is evolved. Chlorine thus liberated is mixed with water vapour and some HCl gas. The gas is bubbled through water in a gas-washer to dissolve out accompanying HCl gas and then through concentrated H_2SO_4 to remove the moisture. Finally, chlorine gas is collected in dry gas-jars by the upward displacement of air.

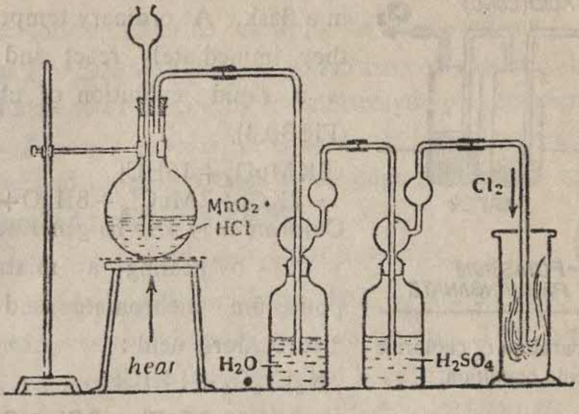


Fig. 30·3 Preparation of chlorine

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

N. B. (i) Chlorine cannot be collected over mercury as it reacts with mercury. It may, however, be collected over saturated brine or hot water in which it is much less soluble, but not over water in which it dissolves rather readily. (2) It is easily seen that the whole of the chlorine present in HCl is not obtained as free chlorine ; a part forms manganous chloride. (3) The action of MnO_2 upon hydrochloric acid takes place, most probably in two stages. Manganese tetrachloride is formed first which decomposes to give chlorine :

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O \; ; \; MnCl_4 = MnCl_2 + Cl_2.$$

Very often, a mixture of sodium chloride and concentrated sulphuric acid, instead of HCl, is heated with manganese dioxide to produce chlorine. It fact, sodium chloride and sulphuric acid produce HCl which is oxidised.

$$2Na\overset{-1}{Cl} + 3H_2SO_4 + \overset{+4}{Mn}O_2 = 2NaHSO_4 + \overset{+2}{Mn}SO_4 + 2H_2O + \overset{0}{Cl_2}$$

(ii) A very convenient and handy method for preparing chlorine consists in the dropwise addition of concentrated hydrochloric acid to powdered potassium permanganate in a flask. At ordinary temperature they immediately react and there is a rapid evolution of chlorine (Fig 30.4).

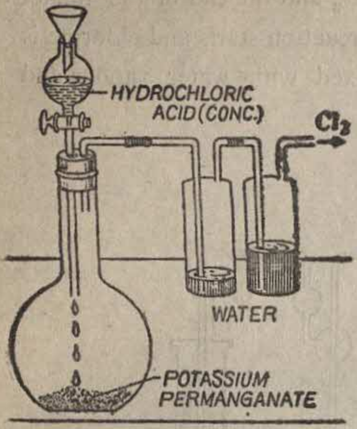


Fig. 30·4. Preparation of cholorine under cold condition.

$$2KMuO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Chlorine may also be generated :

(a) by heating a mixture of potassium dichromate and conc. hydrochloric acid :

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O ;$$

(b) by the action of dilute acid on bleaching powder at the room temperature :

$$Ca(OCl)Cl + 2HCl = CaCl_2 + H_2O + Cl_2 ;$$

(c) by the electrolysis of many metallic chlorides in the fused state, e.g., NaCl, AgCl etc. pure chlorine is obtained by the electrolysis of fused pure silver chloride in Jena glass V-tube protected by asbestos, and fitted with a graphite anode and a gas carbon cathode. Chlorine is liberated at the anode.

(d) by heating platinic chloride, or cupric chloride, to 600°C :

$$PtCl_4 = Pt + 2Cl_2 ;\ 2CuCl_2 = Cu_2Cl_2 + Cl_2$$

30·6. Industrial Preparation :—Large-scale supply of chlorine is available as a by product in the electrolytic conversion of sodium chloride to sodium hydroxide and carbonate (vol II). Brine (concentrated NaCl solution) is electrolysed when caustic soda and chlorine are produced.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Cathode : $Na^+ + e = Na$ Anode : $Cl^- - e = Cl$

$2Na + 2H_2O = 2NaOH + H_2$ $Cl + Cl = Cl_2$

Cholorine gas evolved at the anode is led through silica pipes. The pure electrolytic chlorine is liquefied by compression or by cooling by means of solid carbondioxide plus ether. Liquid chlorine is stored and transported in special steel cylinders.

Previously, chlorine used to be produced on a large scale by *Weldon's* or *Deacon's process*, which have now been almost entirely abandoned and replaced by the electrolytic process mentioned above.

In *Deacon's procesv*, hydrogen chloride is oxidised by air to chlorine and water in pressence of cupric chloride catalyst at the optimum temperature of 450°C.

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

In *Weldon's process*, conc. HCl is heated with pyrolusite in stone-ware vessels by means of live steam. The evolved chlorine passes out through a stone pipe and is collected :

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The success of the method depended on the recovery of the oxidising agent MnO_2, which could be used again.

30·7. Properties of chlorine. *Physical properties* :—Chlorine is a greenish-yellow gas with a characteristic pungent suffocating smell. It is two and a half times heavier than air and is only slighly soluble in water ; the solution is called 'chlorine-water'. It is very poisonous and corrodes skin forming blisters. The gas can be easily liquefied to an amber-yellow liquid (b.p. − 35°C) by cooling and compression.

Chemical Properties :—(1) Chlorine is a highly reactive element. It combines directly with nearly all elements—metals and non-metals —forming their chlorides, the principal exceptions being carbon, nitrogen and oxygen.

Iron, aluminium, zinc, mercury, copper etc. are attacked by chlorine and their chlorides are formed, the reactions being facilitated at elevated temperatures.

$$2Fe + 3Cl_2 = 2FeCl_3 \; ; \; Cu + Cl_2 = CuCl_2$$

$$Hg + Cl_2 = HgCl_2 \; ; \; 2Au + 3Cl_2 = 2AuCl_3$$

$$Zn + Cl_2 = ZnCl_2 \; ; \; 2Al + 3Cl_2 = 2AlCl_3.$$

Phosphorus, antimony, arsenic, sodium etc. spontaneously ignite in contact with chlorine and produce their chlorides.

$$2P + 5Cl_2 = 2PCl_5 \; ; \; 2Na + Cl_2 = 2NaCl.$$
$$2Sb + 3Cl_2 = 2SbCl_3 \; ; \; Mg + Cl_2 = MgCl_2.$$
$$2As + 3Cl_2 = 2AsCl_3 \; ; \; 2Bi + 3Cl_2 = 2BiCl_3.$$

chlorine when bubbled through molten sulphur gives sulphur chloride : $2S + Cl_2 = S_2Cl_2$

(ii) *Reaction with hydrogen* :—chlorine has a great affinity for hydrogen. In diffused light, chlorine slowly combines with hydrogen producing hydrogen chloride. In bright sunlight the reaction occurs with explosive violence : $H_2 + Cl_2 = 2HCl$.

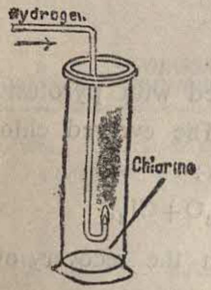


Fig 30·5. Hydrogen burning in chlorine

A burning jet of hydrogen continues to burn with a greenish flame, when introduced in a jar of chlorine, forming hydrogen chloride (Fig 30.5.). A jet of chlorine also burns in a jar of hydrogen.

The reaction between hydrogen and chlorine is rapid even in the dark in presence of activated charcoal—a process of commercial importance.

Because of its great affinity for hydrogen, chlorine extracts out hydrogen from many organic compounds such as hydrocarbons to form hydrochloric acid, with the liberation of carbon with which chlorine does not react. Thus if a filter paper soaked in turpentive be introduced into a jar of chlorine gas, it spontaneously ignites and produces carbon and hydrogen chloride : $C_{10}H_{16} + 8Cl_2 = 10C + 16HCl$. Similarly a lighted candle, when inserted into a jar filled with chlorine gas, continues to burn with a sooty flame :

$$C_xH_y + (y/2)Cl_2 = xC + yHCl.$$

(*iii*) *Reaction with water* :—The yellowish aqueaus solution of chlorine, known as chlorine water, contains a mixture of hydrochloric and hypochorous acids, HOCl, the latter being unstable, liberates nascent oxygen on keeping and particularly in sunlight. Hence the oxidising and bleaching properties of chlorine water :

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl \; ; \; HOCl \rightarrow HCl + O$$

In bright sunlight chlorine decomposes water liberating oxygen, the reaction is reversible :

$$2H_2O+2Cl_2=4HCl+O_2.$$

A saturated solution of chlorine, cooled to 0°, deposits crystals of chlorine hydrate, $Cl_2, 6H_2O$.

(*iv*) *Reaction with alkalis* :—(a) With dilute alkali solutions (i.e., NaOH, KOH or $Ca(OH)_2$) in the cold, chlorine produces chloride and hypochlorite, provided the alkali solution is in excess. For example,

$$Cl_2+H_2O=HCl+HOCl$$

$$\underline{HCl+HOCl+2NaOH=NaCl+NaOCl+H_2O}$$

i.e., $$\underset{\text{(sodium hypochlorite)}}{Cl_2+2NaOH=NaCl+NaOCl+H_2O}$$

similarly, $$\underset{\text{(cal. hypochlorite)}}{2Cl_2+2Ca(OH)_2=CaCl_2+Ca(OCl)_2+2H_2O}$$

(b) With excess of chlorine, especially with hot and concentrated alkali solution, chlorides and chlorates are produced, through the intermediate formation of hypochlorites :

$$6NaOH+3Cl_2=3NaCl+3NaOCl+3H_2O$$

$$\underline{3NaOCl=NaClO_3+2NaCl}$$

i.e., $$\underset{\text{(sodium chlorate)}}{6NaOH+3Cl_2=5NaCl+NaClO_3+3H_2O}$$

similarly, $$\underset{\text{(cal. chlorate)}}{6Ca(OH)_2+6Cl_2=5CaCl_2+Ca(ClO_3)_2+6H_2O}$$

(c) When chlorine gas is passed over dry slaked lime at about 40°C, bleaching powder is formed :

$$\underset{\text{(bleaching powder)}}{Cl_2+Ca(OH)_2=Ca(OCl)Cl+H_2O}$$

(d) With calcium oxide at a red heat, chlorine react to form calcium chloride and oxygen :

$$2CaO+2Cl_2=2CaCl_2+O_2.$$

(*v*) *Oxidising action of chlorine* :—Chlorine behaves as a powerful oxidising agent. Chlorine exhibits its oxidising power (a) by addition of chlorine, (b) by removal of hydrogen or (c) by addition of oxygen to a compound. For example, ferrous salts, stannous salts, are oxidised to ferric and stannic salts by addition of chlorine :

$$2FeCl_2 + Cl_2 = 2FeCl_3 \; ; \; SnCl_2 + Cl_2 = SnCl_4.$$

Chlorine oxidises hydrogen sulphide, hydrogen iodide, ammonia etc. by removing hydrogen from these compounds :

$$H_2S + Cl_2 = S + 2HCl \; ; \; 2HI + Cl_2 = I_2 + 2HCl \; ;$$

$2NH_3 + 3Cl_2 = N_2 + 6HCl$, if chlorine be in excess, nitrogen trichloride is formed : $NH_3 + 3Cl_2 = NCl_3 + 3HCl$.

In presence of water, chlorine oxidises sulphurous acid to sulphuric acid and potassium sulphide to potassium sulphate by actually adding oxygen to these compounds :

$$H_2SO_3 + Cl_2 + H_2O = H_2SO_4 + 2HCl$$

$$K_2S + 4Cl_2 + 4H_2O = K_2SO_4 + 8HCl.$$

Chlorine replaces bromine and iodine from bromides and iodides :

$$2KBr + Cl_2 = 2KCl + Br_2 \; ; \; 2KI + Cl_2 = 2KCl + I_2.$$

(*vi*) *Addition and substitution reactions* :—Chlorine combines directly with unsaturated compounds such as carbon monoxide, sulphur dioxide and unsaturated hydrocarbons in presence of sunlight. These are "*additive reactions*".

$$CO + Cl_2 = COCl_2 \text{ (carbonyl chloride)}$$

$$SO_2 + Cl_2 = SO_2Cl_2 \text{ (sulphuryl chloride)}$$

$$C_2H_4 + Cl_2 = C_2H_4Cl_2 \text{ (ethylene dichloride)}$$

With saturated hydrocarbons, however, chlorine replaces hydrogen when exposed to light, forming *substitution* products (see reactions of methane, vol II).

$$CH_4 + Cl_2 = CH_3Cl + HCl$$

(*vii*) *Bleaching action of chlorine* :—Moist chlorine bleaches vegetable colours by oxidation, dry chlorine does not bleach. The nascent oxygen liberated by its action on water is responsible for the bleaching action of chlorine.

A printed page of a book will not be bleached by chlorine because the carbon present in printer's ink is unaffected by dry or moist chlorine.

30·8. Tests :—(i) Chlorine can be detected by its greenish-yellow colour, peculiar irritating smell and bleaching properties. (ii) The presence of chlorine may also be detected by putting a moist starch-iodide paper in the gas ; the paper immediately turns blue.

30·9. Uses :—(i) Chlorine is widely used as a bleaching agent for bleaching paper pulp, cotton and linen textiles, (ii) It is used as a disinfectant for purifying water for domestic purposes, (iii) It is also extensively used for manufacture of bleaching powder, hydrochloric acid, bromine, chlorates, solvents (CCl_4 etc.), plastics (such as PVC) and many metallic and non-metallic chlorides, such as $AlCl_3$, $MgCl_2$, PCl_5 etc. (iv) Chlorine is used as a poison gas, and for making some poisonous gases, used in war, such as, phosgene gas, mustard gas and chloropicrin. (v) Insecticides like DDT, gammaxene, antiseptics like dettol, refrigerants like 'Freons' require chlorine for their preparation.

General method of preparation of halogens :—The three halogens, chlorine, bromine and iodine may be prepared by the same general method, i.e., by heating the appropriate halide with manganese dioxide and concentrated sulphuric acid :

$$MnO_2+2NaX+3H_2SO_4=MnSO_4+2NaHSO_4+2H_2O+X_2$$

Where X = Cl, Br or I. Fluorine, as already discussed, cannot be isolated by this general method.

BROMINE

Formula Br_2, Atomic number 35, Atomic weight 79·9, Electronic configuration [Ar] $3d^{10}$ $4s^2 4p^5$.

30·10. History and occurrence :—In 1825, bromine was discovered by Balard by chlorinating the mother liquor left after the separation of common salt from sea water by evaporation.

Bromine does not occur free in nature. It occurs only in combination—as bromides of sodium, potassium, mangnesium and calcium in sea water ; in mineral water, and in the stassfurt salt deposits.

30.11. Preparation : *Laboratory method* :—In the laboratory bromine is always prepared by distilling a mixture of potassium bromide and manganese dioxide (1:5) with moderately conc. sulphuric acid in a glass retort, the end of which communicates with a glass receiver kept cold with ice-water (Fig 30.6). Bromine distils and condenses as a dark red heavy fuming liquid in the receiver :

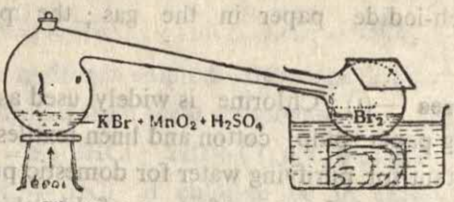


Fig. 30·6. Preparation of bromine

$$MnO_2 + 2KBr + 3H_2SO_4 = MnSO_4 + 2KHSO_4 + Br_2 + 2H_2O.$$

It is purified by distillation over potassium bromide which will remove any traces of chlorine. It may be dried by treatment with quicklime or anhydrous calcium bromide.

Bromine may also be prepared by passing chlorine into a strong solution of a bromide :

$$2KBr + Cl_2 = 2KCl + Br_2.$$

30·12. Industrial preparation of Bromine :—On a large scale bromine is prepared either from carnallite ($KCl, MgCl_2, 6H_2O$) of stassfurt deposit, which contains $MgBr_2$ as impurity or from sea water.

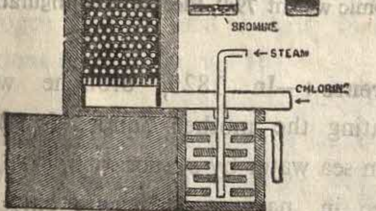


Fig. 30·7. Mannfacture of Bromine from Bitteru

(i) From carnallite :— This is the most important source of bromine. The hot solution of carnallite deposits crystals of potassium chloride on cooling and the mother liquor, called *bittern*, contains appreciable quantities of $MgBr_2$. The mother liquor at a temperature of about 50°C is allowed to run down a tower which is packed with earthenware balls (Fig 30.7.) and connected with a tank below. Streams of chlorine gas and steam are sent into the tower from the bottom which rise upwards. Chlorine expels bromine from mangnesium bromide :

$$MgBr_2+Cl_2=MgCl_2+Br_2.$$

The bromine vapaur leaves the tower by an outlet at the top and is condensed in a spiral earthenware condenser. Any vapour of bromine that escape condensation is absorbed by iron fillings, kept in a small tower, forming bromides of iron.

The spent liquor flowing into the tank carries with it some bromine ; this is recovered by passing in a current of steam which takes it back into the tower.

(ii) **From Sea-water** :—In America, bromine is extracted straight from sea-water, to meet the increasing demand of bromine. Ocean-water is first acidifind with sulphuric acid at PH 3·5 ; this reduces the solubility of bromine. Chlorine gas is then passed through the water and bromine is expelled : $MgBr_2+Cl_2=MgCl_2+Br_2$, Air is blown through the water to remove the liberated bromine which is absorbed in caustic soda or sodium carbonate solution : $3Br_2+6NaOH=NaBrO_3+5NaBr+H_2O$. On acidification of this solution, bromine is regenerated which is collected by distillation :

$$NaBrO_3+5NaBr+3H_2SO_4=3Na_2SO_4+3Br_2+3H_2O$$

1800 gallous of Sea-water are treated to obtain 1 lb. of bromine. More than 50,000 tons of Br_2 are produced annually in U.S.A.

30·13. Properties of Bromine : *Physical properties* :—Bromine is a deep red, heavy fuming liquid with an irritating smell and corrosive properties. Its sp. gr. is 3·14 ; it boils at 59°C, it is the only non-metal which is liquid at the ordinary temperature. It is highly poisonous and inhaling the vapour may be fatal. The bromine vapour attacks the eyes and mucous membranes and the liquid inflicts severe burns on the skin. It is adpperciably soluble in water giving a reddish coloured solution, known rs "Bromine-water". It is also soluble in organic solvents like CS_2, CCl_4, $CHCl_3$ etc.

Chemcial properties :—Bromine resembles chlorine in its chemical properties, although it is less reactive.

(i) It combines with various metals and non-metals directly giving the respective bromides. Bromine combines spontaneously and with deflagration with phosphorus (white or red), arsenic, antimony and potassium and with many other elements when warmed.

$$2P+3Br_2=2PBr_3\ ;\ 2K+Br_2=2KBr$$
$$2P+5Br_2=2PBr_5\ ;\ 3Fe+4Br_2=FeBr_2+2FeBr_3$$
$$2As+3Br_2=2AsBr_3\ ;\ Hg+Br_2=HgBr_2$$

(ii) Bromine reacts directly with hydrogen slowly in sunlight, rapidly when heated, but less vigorously than chlorine :

$$H_2+Br_2=2HBr.$$

Platinum is a suitabe catalyst for the reaction.

(iii) The reddish-coloured aqueous solution of bromine, called bromine water, is fairly stable ; it contains only small quantities of hypobromous and hydrobromic acids. it bright sunlight bromine reacts with water, liberating oxygen :

$$2Br_2+2H_2O=4HBr+O_4.$$

Bromine water, on cooling, yields red crystalline bromine hydrate, Br_2, $8H_2O$.

(iv) The reactions of bromine with alkalis are parallel to those of chlorine, yielding *bromide* and *hypobromite* with a cold solution of an alkali, and *bromide* and *bromate* with the hot and concentrated solution of an alkali.

$$Br_2+2NaOH\ (\text{cold})=NaBr+NaOBr+H_2O$$
$$3Br_2+6NaOH\ (\text{hot \& concn.})=5NaBr+NaBrO_3+3H_2O$$

(v) Like chlorine, bromine behaves as a powerful oxidising agent. It liberates iodine from hydrogen iodide, sulphur from hydrogen sulphide and converts sulphurous acid to sulphuric acid, arsenous to arsenic acid. It can displace iodine from potassium iodide.

$$2HI+Br_2=2HBr+I_2\ ;\quad H_2SO_3+Br_2+H_2O=H_2SO_4+2HBr$$
$$H_2S+Br_2=2HBr+S\ ;\quad 2KI+Br_2=2KBr+I_2$$

Bromine cannot displace chlorine from chlorides.

(vi) Bromine unites with unsaturated organic compounds.

$$\underset{\text{(ethylene)}}{C_2H_4} + Br_2 = \underset{\text{(ethylene dibromide)}}{C_2H_4Br_2}$$

(vii) Bromine water has only feeble bleaching properties ; it bleaches litmus and turns starch paper orange-yellow.

30·14. Tests :—(i) Bromine is easily recognised from its red colour and irritating smell. (ii) If bromine water is shaken with CS_2, the carbon-disulphide turns yellowish-brown. (iii) A wet starch-iodide paper turns blue in bromine gas.

30·15. Uses :—(i) A considerable portion of bromine is used in making ethylene dibromide, $C_2H_4Br_2$ extensively used as an antiknock, (ii) Bromine is also required for perparation of different bromides used in medicine and in photography (AgBr), (iii) It is used in the manufacture of certain coal-tar dyes, in making tear gases and as a disinfectant, (iv) It is also used in chemical laboratories in various organic synthesis and as an oxidising agent.

IODINE

Formula I_2, Atomic number 53, Atomic weight 126·9. Electronic Configuration [Kr] $4d^{10}5s^25p^5$.

30·16. Occurrence :—Iodine is a rather rare element and occurs in the combined state as iodide in sea-water (about ·001 percent). Certain deep sea-weeds extract iodine from sea-water. The ash obtained by burning such sea-weeds is called *kelp*, from which Courtois (1812) discovered the element. Some sodium iodate ($NaIO_3$) is present, to the extent of 0·2 percent, with chile saltpetre called *caliche*. This is an important source of iodine. Traces of iodine are present as thyroxine in the thyroid glands ; it is also present in milk, cod-liver oil, green vegetables etc. in minute amounts as organic-iodine compounds.

30·17. Preparation : *Laboratory method* :—In the laboratory, iodine is prepared by the same method as applied for bromine and chlorine. A mixture of potassium iodide, manganese dioxide and moderately concentrated (50%) sulphuric acid is heated in a glassstoppered retort. The neck of the retort enters into a well-cooled receiver. The violet vapours of iodine are evolved which pass into the receiver and condense there as beautiful shining black crystals :

$$MnO_2+2KI+3H_2SO_4=I_2+2KHSO_4+MnSO_4+2H_2O.$$

Iodine may also be obtained by passing chlorine gas into a eoncentrated solution of sodium or potassium iodide :

$$2KI+Cl_2=2KCl+I_2.$$

Crude iodine may be purified by subliming with solid potassium iodide carefully and collecting the dark coloured shining crystals of iodine in a cooled receiver.

30·18. Industrial preparation :—The chief sources are (i) Deep sea-weeds, (ii) Caliche and (iii) Petrolium brines. There are different methods for preparing iodine on a large scale depending upon the source.

(*i*) *From kelp* :—The ash from burnt sea-weeds, i.e., kelp, contains sodium and potassium iodides with other salts. It is lixiviated with hot water and the insoluble matter is filtered off. The solution is then concentrated and cooled when less soluble sulphates, carbonates, chlorides etc. of alkali metals crystallise out and the very soluble potassium and sodium iodides remain in the mother liquor. The precipitates are filtered off and the mother lipuor is mixed with conc. H_2SO_2 and MnO_2 and distilled from cast iron pots when iodides are oxidised to iodine. The vapours are led into earthenware bottle-shaped receivers called *aludels* where iodine is collected (Fig 30.8.). The iodine is purified by sublimation.

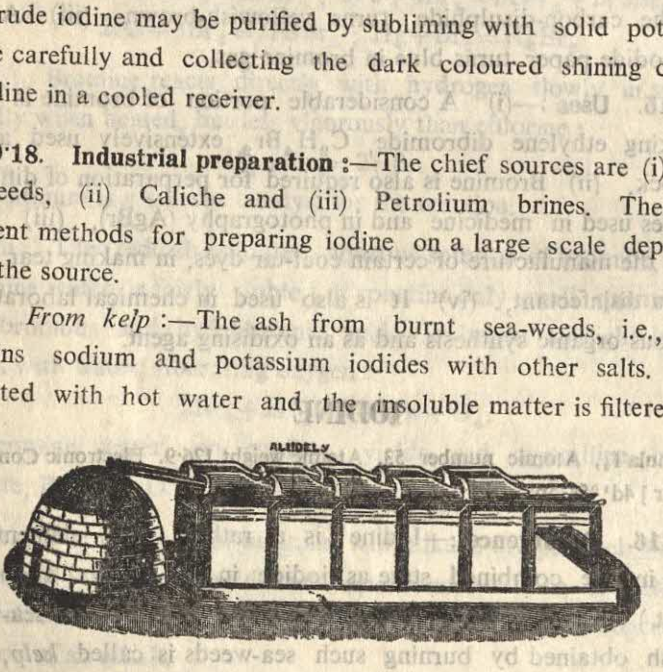


Fig. 30·8. Preparation of iodine from kelp (*ii*) *From caliche* :—The crude chile saltpetre, caliche contains some sodium iodate with sodium nitrate. The mother liquor, obtained after the removal of sodium nitrate by crystallisation, contains about 2∼3 gm of $NaIO_3$ per litre. This is treated with calculated amount of sodium bisulphite solution which precipitates iodine. The acid sulphite sets free iodic acid, and reduces five-sixths of it to hydrogen iodide :

$$NaIO_3 + NaHSO_3 = Na_2SO_3 + HIO_3$$
$$HIO_3 + 3Na_2SO_3 = HI + 3Na_2SO_4.$$

The hydriodic acid and iodic acid then react precipitating iodine :

$$5HI + HIO_3 = 3I_2 + 3H_2O.$$

The iodine is separated from the solution, dried and sublimed.

(*iii*) *From Petrolium brines* :—Brive obtained from petrolium well in south california, U.S.A., contains 60-70 parts of iodine in the form of sodium iodide per million parts of brine—recently, this has become an important source of iodine. The brine is treated with sodium nitrite to oxidise the iodide to iodine in presence of dilute H_2SO_4.

$$2NaNO_2 + 2NaI + H_2SO_4 = I_2 + 4NaHSO_4 + 2NO + 2H_2O.$$

The solution bacomes yellow on account of liberation of iodine which remains in very dilute solution. The iodine is absorbed by activated charcoal. The charcoal is filtered and treated with hot caustic soda to dissolve the iodine. The solution is then acidified to produce the iodine.

$$3I_2 + 6NaOH = 5NaI + NaIO_3 + 3H_2O$$
$$5NaI + NaIO_3 + 3H_2SO_4 = 3I_2 + 3Na_2SO_4 + 3H_2O.$$

Purification : Commercial iodine may contain ICl, IBr, and ICN. These impurities are removed by heating a mixture of the crude iodine and potassium iodide when the impurities react with potassium iodide and pure iodine sublimes :

$$ICl + KI = KCl + I_2.$$

30·19. Properties of Iodine : *Physical properties* :—Iodine occurs as shining dark grey crystals with a metallic lustre. It forms violet vapours when heated and it readily sublimes to a grey solid. The solid has a density of 4·1 gm per c.c. The vapour density conforms to the formula I_2 upto 700°C, above which thermal dissociation occurs, $I_2 \rightleftharpoons 2I$. Iodine is very slighly soluble in water, but it readily dissolves in aqueous KI giving a brown solution, with the formation of potassium tri-iodide : $KI + I_2 \rightleftharpoons KI_3$. It is also soluble in many organic solvents like CS_2, $CHCl_3$, C_6H_6, ether etc. In water, ether and alcohol iodine forms brown solution, in benzene and chloroform purple solution and in carbondisulphide a violet solution.

Chemical properties :—Although less reactive than other halogens, iodine resembles them in chemical properties. Thus—

(i) Iodine readily combines with many metals forming iodides. Mercury when triturated with iodine yields either mercurous iodide, Hg_2I_2 or mercuric iodide, HgI_2, according to the proportions taken. The reaction with potassium proceeds with explosive violence.

$$Hg + I_2 = HgI_2 \; ; \; 2K + I_2 = 2KI.$$

Like chlorine, iodine vapours support the combustion of white phosphorus, arsenic, antimony etc., though less energetically :

$$2P + 3I_2 = 2PI_3.$$

Hydrogen and iodine unite at high temperatures to give hydrogen iodide, but the reaction is incomplete and reversible :

$$H_2 + I_2 \rightleftharpoons 2HI.$$

Iodine forms interhalogen compounds by uniting with other halogens, e.g., IF_5, ICl, ICl_3, IBr etc. In these compounds, iodine extibits a mild electropositive character.

(ii) The reactions of iodine with alkalis are similar to those of chlorine and bromine ;

(a) With cold dil. NaOH ; $I_2 + 2NaOH = NaI + NaIO + H_2O$
(sodium hypoiodite)

(b) With hot conc. NaOH ; $3I_2 + 6NaOH = 5NaI + NaIO_3 + 3H_2O$
(sodium iodate)

The hypoiodites are rather unstable and readily change to iodide and iodates :

$$3NaIO = 2NaI + NaIO_3.$$

(iii) Iodine is a mild oxidising agent. Sulphur separates when hydrogen sulphide is passed into a suspension of iodine in water. It oxidises sulphurous acid to sulphuric acid, arsenious acid to arsenic acid, stannous chloride to stannic chloride :

$$I_2+H_2S=2HI+S$$

$$I_2+H_2SO_3+H_2O=H_2SO_4+2HI$$

$$I_2+H_3AsO_3+H_2O=H_3AsO_4+2HI$$

$$I_2+SnCl_2+2HCl=SnCl_4+2HI$$

(iv) Iodine cannot replace chlorine or bromine from chlorides and bromides. But iodine can liberate chlorine and bromine from chlorates and bromates.

$$2KClO_3+I_2=2KIO_3+Cl_2\ ;\ 2KBrO_3+I_2=2KIO_3+Br_2.$$

(v) Iodine reacts quantitatively with sodium thiosulphate solution—thiosulphate is oxidised to tetrathionate.

$$\underset{\text{(sod. thiosulphate)}}{2Na_2S_2O_3}+I_2=2NaI+\underset{\text{(sod. tetrathionate)}}{Na_2S_4O_6}$$

This reaction is used for the volumetric estimation of iodine.

(vi) Since iodine is practically insoluble in water, it has no bleaching properties.

(vii) Unlike other halogens, iodine may be oxidised to iodic acid by concentrated nitric acid :

$$3I_2+10HNO_3=6HIO_3+10NO+2H_2O.$$

(viii) Iodine gives a deep blue colour with starch solution. The blue product is probably an adsorption complex of starch and iodine.

30·20. Tests :—(i) One heating, iodine gives distinct violet vapour, (ii) it produces violet colour when dissolved in CS_2, (iii) iodine gives a blue colour with starch solution, it is a very sensitive test for iodine, (iv) it produces yellow crystals of iodoform of characteristic smell, when warmed with ethyl alcohol and caustic soda.

30·21. Uses :—(i) Iodine is used in the preparation of iodoform (CHI_3) used as an antiseptic and tincture of iodine (a solution of iodine in potassium iodide and rectified spirit) used as a disinfectant. (ii) It is also used for preparing some dyes, drugs and potassium iodide. (iii) In the chemical laboratories, iodine is used in volumetric analysis and in organic synthesis.

HALOGEN HYDRACIDS

All the halogens form hydrides, the affinity of the halogens for hydrogen diminishes with the atomic number from fluorine to iodine. The hydrides of the halogens in aqueous solution are acids, but in the anhydrons state they are covalent compounds, $H-F$, $H-Cl$, $H-Br$, $H-I$. The halogen hydracids are, hydrofluoric acid, hydrochloric acid, hydrobromic acid and hydriodic acid. They can be represented by HX, where X = F, Cl, Br or I.

HYDROFLUORIC ACID, HF

30·22. Preparation of Hydrofluoric acid :—An aqueous solution of hydrofluoric acid is prepared by distilling in a lead resort powdered flluorspar, CaF_2 ; with 90 percent. Sulphuric acid, and dissolving the gas evolved in water contained in a lead receiver : The solution is kept in bottle of wax, gutta-percha or polythene.

$$CaF_2 + H_2SO_4 = CaSO_4 + HF.$$

The anhydrous acid is comonly prepared by distilling dry potassium hydrogen fluoride, KHF_2, called *Fremy's Salt*, from a platinum retort, employing a platinum condenser and a platinum receiver, cooled in freezing mixture. Copper apparatus may be subtituted for the expensive platinum. KHF_2 is decomposed by heat, liberating hydrofluoric acid gas which condenses to a liquid in the receiver.

$$KHF_2 = KF + HF.$$

30·23. Properties :—(i) Anhydrous hydrofluoric acid is a colourless, strongly fuming liquid, boiling at 19·5°C. Hydrogen fluoride is very poisonous and dangerous to manipulate. Rubber gloves are used in working with the acid. It causes painful and dangerous wounds on the skin, which heal if immediately treated with magnesium or calcium hydroxide.

(ii) In the anhydrous condition, the acid is non-electrolyte. The liquid acid and its vapour at low temperatures remain associated and consists of polymeric forms, $(HF)_x$, whereas at 100°C, the vapour density corresponds to the molecular formula HF. The association of hydrogen fluoride molecules is attributed to hydrogen bonding.

(iii) The liquid acid destroys rubber and organic substances. and in presence of a trace of moisture the liquid attacks glass violently, and has action on all but the noble metals. Gaseous hydrogen fluoride is absorbed by dry sodium fluoride :

$$HF + NaF = NaHF_2.$$

(iv) It is completely miscible with water, the aqueous solution is conducting and behaves as a weak acid. The acid attacks all but noble metals yielding metallic flluorides and hydrogen :

$$Fe + 2HF = FeF_2 + H_2.$$

(v) The most characteristic property of the acid is its action on glass yielding a colourless and pungent gas silicon tetrafluoride and ultimately hydro-fluosilicic acid :

$$SiO_2 + 4HF = SiF_4 + 2H_2O \; ; \; SiF_4 + 2HF = H_2SiF_6.$$

The *etching af glass* is bassed on this reaction. The acid is therefore kept in gutta-percha or glass vessels coated internally with paraffin.

Both moist gaseous HF and the aqueous solution are used for etching glass. Etching with solution is clear and transparent, but that with the gas appears opaque, frosty and dull.

(vi) If aqueous hydrofluoric acid is neutralised with potassium hydroxide, the crystalline salt KF is obtained on evaporation. If twice the equivalent proportion of hydrofluoric acid is added to potassium hydroxide, the solution on evaporation deposits crystals of the acid salt KHF_2. The aqueous acid reacts with boric acid to form hydrofluoboric acid :

$$B(OH)_3 \text{ (boric acid)} + 4HF = HBF_4 + 3H_2O.$$

30·24. Tests :—(i) The acid is easily detected by its etching action on glass.

(ii) Fluorides are detected by heating them with strong sulphuric acid in a glass tube (which contains silica), when silicon tetrafluoride is evolved A drop of water on a glass rod, on exposure to the gas, turns opaque due to the formation of insoluble silicic acid,

$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$; $4HF + SiO_2 = SiF_4 + 2H_2O$

$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3$.

30·25. Uses :

(i) The hydrofluoric acid is used in etching designs of glass and marks and graduations of glass apparatus. (ii) Sodium and Zinc fluorides are used in the preservation of wood, (iii) SnF_2 is often used as a constituent of tooth paste for protection of dental enamal. The *fluorides* are stable salts of hydrofluoric acid and are analogous to chlorides, but unlike the latter, many of them combine with HF to form acid fluorides : $KF + HF = KHF_2$. Acid ammonium fluoride is obtained when normal ammonium fiuoride is heated : $2NH_4F = NH_3 + NH_4HF$. Silver fluoride, AgF is soluble in water (AgCl, AgBr and AgI are insoluble), and calcium fluoride, CaF_2 is insoluble in water ($CaCl_2$, $CaBr_2$ and CaI_2 are soluble).

HYDROCHLORIC ACID, HCl

30·26. Preparation of Hydrochloric acid :

(i) In the laboratory, hydrogen chloride gas is prepared by gently heating a mixture of sodium chloride and fairly concentrated sulphuric acid in a flask fitted with a thistle funnel and a delivery tube. The reaction takes place in two stages :

(i) $NaCl + H_2SO_4 = NaHSO_4 + HCl$ (150° – 200°)

(ii) $NaCl + NaHSO_4 = Na_2SO_4 + HCl$ (over 500°)

The issuing gas may be dried by passing through concentrated H_2SO_4 and collected by the

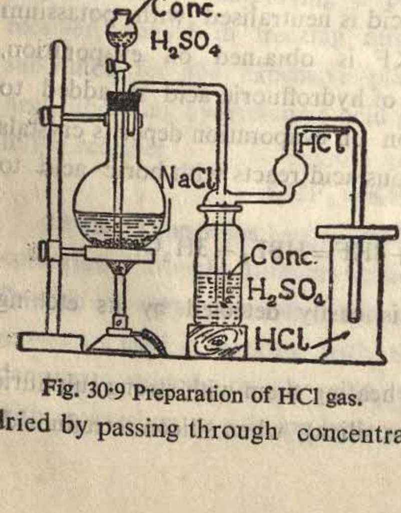


Fig. 30·9 Preparation of HCl gas.

upwar displacement of air, or over mercury (Fig. 30.9). It should not be dried over phosphorus pentoxide, as it is absorbed according to reaction : $2P_2O_5 + 3HCl = POCl_3 + 3HPO_3$. It is not collected over water as it is highly soluble in water.

In the gaseous state it is called hydrogen chloride to distinguish it from its aqueous solution which is called "*hydrochloric acid*". To prepare aqueous hydrochloric acid, the gas produced in the flask is first allowed to pass through an empty bottle and then led into water through an inverted funnel which dips just below the surface of water in a beaker—the gas dissolves in water, yieldding an aqueous solution of hydrochloric acid (Fig 30·10). This device is necessary to prevent the back-suction of water into the reaction vessel. Hydrogen chloride is extremely soluble in water. When it comes in contact with water, it dissolves rapidly creating a partial vaccum, the water then rises up. The funnel rim then comes above the water surface and air enters ; the water falls back. In this way it prevents back suction.

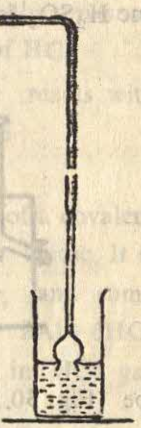


Fig 30·10 Anti-suction device.

The empty bottle is an additional precaution to prevent water running directly into the reaction vessel.

(ii) The purest hydrogen chloride is made by the action of water on silicon tetrachloride ;

$$SiCl_4 + 2H_2O = SiO_2 + 4HCl.$$

(iii) A regulated supply of hydrogen chloride may be conveniently obtained by dropping conc. H_2SO_4 upon cone. hydrochloric acid taken in a flask (Fig 30·11) ; when the evolution of gas takes place without application of heat.

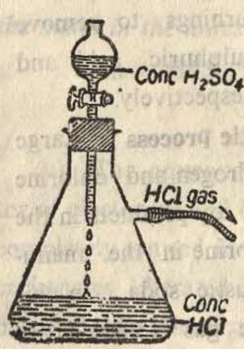


Fig 30·11. Preparation of HCl at room temp.

30·27. Industrial preparation of HCl :

Hydrochloric acid is obtained commercially either as a by product in the manufacture of salt cake from sodium chloride, or synthetically from hydrogen and chlorine.

(i) **From Common salt** : This process of manufacture of HCl is the same laboratory process on a large scale. Common salt and conc H_2SO_4 is heated in a cast iron vessel provided with a delivery pipe (Fig 30.12). The evolved hydrogen chloride is absorbed in water in a set of absorbers made of clay with acid-proof glaze. The product may be purified by distilling over a mixture of barium chloride and copper turnings to remove carried over sulphuric acid and ferric chloride respectively.

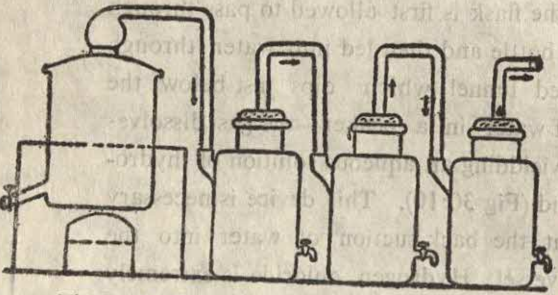


Fig 30.12. Manufacture of HCl from NaCl

(ii) **Synthetic process** : Large quantities of hydrogen and chlorine are available as by-products in the electrolysis of brine in the manufacture of caustic soda. In this proces, chlorine gas is allowed to burn from a jet in an atmosphere of hydrogen in a silica chamber (Fig 30·13). $H_2 + Cl_2 = 2HCl$. The hydrogen chloride produced comes out through an outlet at the top. It is cooled and then absorbed in distilled water in an absorption tower. The hydrochloric acid formed is pure and concentrated.

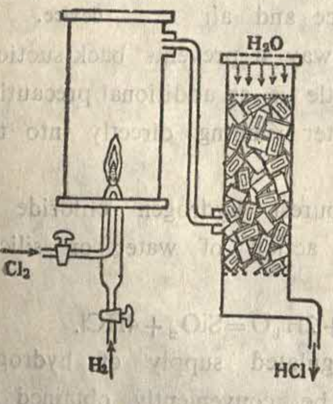


Fig.30·13. HCl by Synthetic Process.

30·28. Properties of HCl :

(i) Hydrogen chloride is a colourless gas with a choking smell. It fumes in moist air. It is 1·27 times heavier than air and is neither combustible nor a supporter of combustion.

(ii) Hydrogen coloride gas is highly soluble in water and the aqueous solution is "hydrochloric acid". when any solution of hydrogen chloride is distilled, the ultimate residue is the *constant boiling mixture*, b.pt. 110°C, containing 20·24 per cent of HCl.

(iii) In presence of moisture, hydrogen chloride reacts with ammonia to produce white fumes of ammonium chloride :

$$HCl+NH_3=NH_4Cl.$$

(iv) Liquid hydrogen chloride has the properties of a covalent compound, it does not conduct electricity, and is not acidic. It is without action on zinc, magnessium, calcium oxide, and some carbonates. Aluminium, however, dissolves in it : $2Al+6HCl=2AlCl_3+3H_2$. Metallic sodium and potassium burn in HCl gas on heating to form NaCl and KCl :

$$2Na+2HCl=2NaCl+H_2.$$

Many other metals when heated decompose gaseous hydrogen chloride, liberating hydrogen and forming the chloride *containing the metal in the lowest (ous) state of valency.*

$$\underset{\text{(stannous chloride)}}{Sn+2HCl=SnCl_2+H_2} \;;\; \underset{\text{(ferrous chloride)}}{Fe+2HCl=FeCl_2+H_2}$$

(v) The aqueous solution of hydrochloric acid is a good conductor of electricity and behaves as a strong mono basic acid. It remains completely ionised in solution. It forms salts with bases, decomposes carbonates, liberated hydrogen with metals which are above hydrogen in the electro chemical series. It dissolves magnesium, zinc and iron readily, and tin and aluminium less readily, forming chlorides containing the metal in the lowest state of valency.

$$HCl\rightleftharpoons H^{+}+Cl^{-} \;;\quad CaCO_3+2HCl=CaCl_2+H_2O+CO_2$$

$$HCl+NaOH=NaCl+H_2O \;;\quad Fe+2HCl=FeCl_2+H_2$$

$$CuO+2HCl=CuCl_2+H_2O \;;\quad Sn+2HCl=SnCl_2+H_2$$

Copper slowly dissolves in hot and concentrated acid, and silver is slowly attacked in presence of air only. Noble metals, such as gold, platinum etc., are not attacked by the aid, however, they are dissolved by aqua regia (3 vol. conc. HCl + 1 vol conc. HNO_3).

$$2Cu + 8HCl = H_2 + 2H_3CuCl_4$$
$$4Ag + 4HCl + O_2 = 4AgCl + 2H_2O.$$

(vi) It is readily oxidised to chlorine by $KMnO_4$, MnO_2, bleaching powder, etc. (see preparation of chlorine) : $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$.

(vii) An aqueous solution of hydrochloric acid gives white precipitates with silver, mercurous and lead salts.

$$AgNO_3 + HCl = AgCl + HNO_3 \; ;$$
$$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 + 2HNO_3$$

30·29. Tests :

(i) HCl acid or any metallic chloride yields greenish yellow chlorine gas when heated with MnO_2 and conc. H_2SO_4. (ii) HCl acid or any soluble chloride gives a curdy white precipitate of silver chloride on addition to silver nitrate solution. The ppt. is soluble in ammonia but insoluble in HNO_3.

$$HCl + AgNO_3 = AgCl + HNO_3$$
$$AgCl + 2NH_4OH = Ag(NH_3)_2Cl + 2H_2O$$

30·30. Uses :

Hydrochloric acid has extensive uses, it stands second only to sulphuric acid in its use in industry. It is used (i) in the preparation of some chlorides, (ii) in dying and calico printing, (iii) in medicine, (iv) in cleaning metal sheets befor tinning, galvanising or enamelling, (v) in making glucose from starch, (vi) as a reagent in the laboratory, and (vii) in the preparation of aqua regia.

Chemically pure concentrated hydrochloric acid contains about 38 per ecent HCl (12N) and has a sp. gr. of 1.19.

30·31. Composition and formula of Hydrogen Chloride :

The composition of hydrogen chloride may be determined either by synthetic method or by analytical method. The synthetic method has been described as follows.

Synthetic Method : Two cylindrical glass bulbs of exactly equal volumes are connected by a stop-cock (Fig 30.14). At the other ends of each bulb, there is also a stop-cock. The two bulbs are then filled with two gases, pure hydrogen and pure chlorine, one gas in each bulb, at the same pressure The two gases are allowed to mix by opening the central stop-cock and the whole apparatus is kept exposed to diffused sunlight for 2-3 days. The two gases unite to form hydrogen chloride. On opening one of the end stop-cocks under mercury, no cnange of volume takes place, but when opened under water, it rushes up and completely fills both the bulbs, showing that there is no uncombined hydrogen. The aqueons solution is found to be acidic and forms a curdly white precipitate with $AgNO_3$ solution and does not liberate iodine from KI solution. These shows that this is wholly hydrochloric acid and contains no free chlorine. Hence, it is concluded that whole of chlorine and hydrogen have combined. That is.

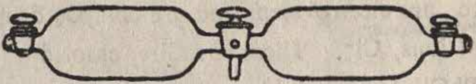


Fig 30·14. Volumetric composition of HCl, synthetic method.

x c.c. of hydrogen and x c.c. of chlorine unite to produce $2x$ c.c. of hpdrogen chloride.

Let x c.c. of any gas contains n molecules (Avogadro).

$\therefore$ n molecules of hydrogen and n molecules of chlorine
$= 2n$ molecules of hydrogen chloride

or, 1 molecule of hydrogen chloride $= \frac{1}{2}$ molecule of $H_2 + \frac{1}{2}$ molecule of Cl_2

or, 1 molecule of hydrogen chloride contains one atom of hydrogen and 1 atom of chlorine.

Hence the formula of hydrogen chloride is HCl. This agrees with the molecular weight 36·5 found experimentally from its vapour density.

Chlorides of metals are the salts of hydrochloric acid. The chlorides of non-metals, for example CCl_4, PCl_3, S_2Cl_2, are covalent compounds. They are usnally colourless liquids and are readily hydrolysed (except CCl_4 which is inert) by water to yield an acid or an acidic oxide, and hydrochloric acid. The chlorides of metals of small atomic volume exerting high valencies, like $SnCl_4$, $PbCl_4$, are also covalent compounds and readily hydrolysed by water.

The chlorides of metals of large atomic volume exerting low valencies, for example the chlorides of sodium, potassium, calcium, magnesium etc., are electrovalent and are composed of metallic ions and chloride ions, Cl^-. These metallic chlorides (except $AgCl$, Hg_2Cl_2 and $PbCl_2$) are soluble in water and are not hydrolysed in solution.

HYDROBROMIC ACID, HBr

Hydrobromic acid and hydriodic acid cannot be prepared by the action of concentrated sulphuric acid upon the corresponding halides as is done in case of hydrochloric acid. For these acids (HBr and HI) are immediately oxidised to bromine and iodine by conc. H_2SO_4.

$$\begin{array}{l} 2KBr+2H_2SO_4=2KHSO_4+2HBr \\ \underline{2HBr+H_2SO_4=Br_2+SO_2+2H_2O} \\ 2KBr+3H_2SO_4=Br_2+SO_2+2KHSO_4+2H_2O \end{array}$$

Similarly ; $2KI+3H_2SO_4=I_2+SO_2+2KHSO_4+2H_2O$.

Hence a different method is required to prepare these two halogen hydracids.

30·32. Preparation : *Laborary method* :—In the laboratory hydrogen bromide is generally prepared by the action of bromine on red phosphorus and the hydrolysis of the resulting phosphorus bromide.

Red, phosphorus and water are taken in a flask fitted with a dropping funnel and a delivery tube. Liquid bromine is then slowly and cautiously added drop by drop from the funnel (Fig 30.15).

Immediate reaction takes place vigorously with the evolution of hydrogen bromide gas.

$$2P + 3Br_2 = 2PBr_3$$
$$PBr_3 + 3H_2O = 3HBr + H_3PO_3$$
$$2P + 5Br_2 = 2PBr_5$$
$$PBr_5 + 4H_2O = H_3PO_4 + 5HBr$$

When the reaction slows down towards the end of the process, the flask is gently heated, if necessary. Hydrogen bromide along with some bromine vapour comes out through the delivery tube and is led through a U-tube containing glass beads covered with moist red phosphorus which absorbs the accompanying bromine vapour. The gaseous hydrogen bromide passes over and is collected by the upward displacement of air in a gas-jar as it is soluble in water. The gas may be dried by passing it through a U-tube containing calcium chloride or bromide and collected over mercury.

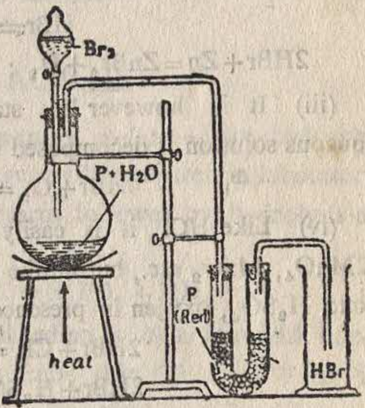


Fig. 30·15. Preparation of hydrogen bromide

Hydrogen bromide may also be prepared by the direct union of hydrogen and bromine. Dry hydrogen is bubbled through warm bromine and the mixture of hydrogen and bromine vapour is then passed over platinised asbestos at 200°C, when they unite to produce hydrogen bromide with the evolution of heat.

$$H_2 + Br_2 = 2HBr \; ; \qquad \Delta H = -8660 \text{ calories.}$$

An aqueous solution of hydrogen bromide, i.e., hydrobromic acid, is prepared by dissolving gaseous hydrogen bromide in water using anti-suction device (as in the case of hydrochloric acid).

An aqueous solution may also be readily obtained by passing hydrogen sulphide or sulphur dioxide into bromine covered with water until the whole solution is pale yellow in colour.

$$H_2S + Br_2 = 2HBr + S$$
$$SO_2 + 2H_2O + Br_2 = H_2SO_4 + 2HBr.$$

30·33. Properties :—(i) Hydrogen bromide is a colourless, very heavy, pungent smelling gas which strongly fumes in moist air. It is exceedingly soluble in water, the aqueous solution is hydrobromic acid which is very similar to hydrochloric acid in its properties.

(ii) Hydrobromic acid is a strong monobasic acid, reacts with many metals producing hydrogen and with bases producing salts etc. in the same way as hydrochloric acid.

$$HBr \rightleftharpoons H^+ + Br^-$$

$$2HBr + Zn = ZnBr_2 + H_2 \text{ ; } HBr + NaOH = NaBr + H_2O.$$

(iii) It is however less stable than hydrochlorine acid,—the aqueous solution is decomposed by air in presence of sunlight :

$$4HBr + O_2 = 2H_2O + 2Br_2.$$

(iv) Like HCl, it is easily oxidised by oxidising agents, like $KMnO_4$, MnO_2 etc., but unlike HCl, it is alo oxidised by chlorine, conc. H_2SO_4, oxygen in presence of sunlight etc.

$$2HBr + Cl_2 = 2HCl + Br_2$$

$$2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O$$

30·34. Tests :—(i) Hydrobromic acid or a metallic bromide when heated with concentrated sulphuric acid evolves red vapours of bromine.

(ii) Chlorine water liberates bromine from a solution of HBr or a metallic bromide. If the solution is shaken with a little CS_2, the latter turns yellow by absorbing bromine.

(iii) $AgNO_3$ solution produces a pale-yellow heavy precipitate of AgBr when added to hydrobromic acid or a solution of a metallic bromide. The ppt. is insoluble in HNO_3 but slowly dissolves in ammonia with difficulty.

30.35. Uses :—Hydrobromic acid is used for preparing bromides. Many of the bromides have application in medicine, photography etc. It is also used as a laboratory reagent.

The metallic bromides are stable salts, for the most part soluble in water ; in solution they are not hydrolysed. The bromides of silver, lead and mercurous mercury are insoluble.

Large quantities of hydrogen bromide for the preparation of hydrobromic acid are conveniently made by the action of bromine on benzene in presence of dry aluminium powder, which acts as a catalyst.

$$C_6H_6 + Br_2 = \underset{\text{(bromo benzene)}}{C_6H_5Br} + HBr.$$

HYDRIODIC ACID,HI.

30·36. Preparation : (i) *Laboratory melhod*—Like hydrogen bromide, gaseous hydrogen iodide is generally prepared in laboratory by the action of iodine on red phosphorus followed by hydrolysis of the phosphorus iodite.

$$2P + 3I_2 = 2PI_3 \text{ ; } PI_3 + 3H_2O = H_3PO_3 + 3HI.$$

A mixture of red phosphorus and iodine is taken in a flask filted with a dropping funnel and a delivery tube (Fig 30·16·). Water is then added drop by drop to these mixture from the funnel and the flask is slowly heated. Hydrogen iodide is formed, the gas is passed through a U-tube containing glass beads smeared with moist red phosphorus to remove any unchanged iodine vapour. The hydrogen iodide is then dried by passing it through a bulb of P_2O_5 and finally collceted by the upward displacement of air. The gas attacks mercurty, so its cannot be collected over it.

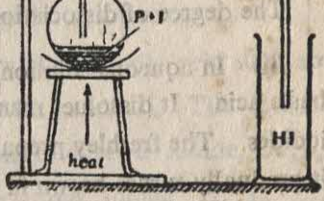


Fig 30·16. Preparation of hydrogen iodide

(ii) Hydrogen iodide may be synthesised by passing a mixture of hydrogen and iodine vapour over heated spongy platinum or platinised asbestos. HI is easily dissociated by heat :

$$H_2 + I_2 \rightleftharpoons 2HI.$$

(ii) Like hydrogen bromide, hydrogen iodide also cannot be prepared by the reaction between potassium (or sodium) iodide and conc. H_2SO_4 and hydrogen iodide is oxidised by conc. H_2SO_4 to iodine. It may, however be prepared by heating potassium iodide with phosphoric acid :

$$3KI + H_3PO_4 = K_3PO_4 + 3HI$$

The aqueous solution of hydrogen iodide is hydriodic acid. This is prepared by the absorption of the gaseous hydrogen iodide in water in the usual way, as in the case of hydrochloric acid and hydrobromic acid.

An aqueous solution of hyhriodic acid upto sp. gr. 1·56 is conveniently obtained by bubbling hydrogen sulphide through a suspension of iodine in water—the precipitated sulphur is filtered off : $H_2S + I_2 = 2HI + S$.

30·37. Properties : (i) Hydrogen iodide is a colourless heavy gas. It fumes in moist air and highy soluble in water. The aqueous solution is hydriodic acid, which resembles hydrochloric and hydrobromic acids in its propertis. But it is less stable than the other two. It undergoes reversible dissociation when heated, or even in presence of sunlight :

$$2HI \rightleftharpoons H_2 + I_2 \text{ ; } \Delta H = +1400 \text{ calories.}$$

The degree of dissociation increases with rise of temperature

(ii) In aqueous solution hydriodic acid haves as a strong monobasic acid. It dissolues many metals and reaets with bases to form iodides. The freshley prepared aqueous solution is colourless, but it gradually turnes brown in sunlight and air, owing to separation of free iodine : $4HI + O_2 = 2H_2O + 2I_2$.

(iii) It behaves as a powerful reducing agent and is a much more active reducing agent that hydrobromic acid. It is oxisdised to iodine by a large number of oxidising agents, such as oxygen, hydrogen peroxide, chlorine, bromine, nitric acid, sulphuric acid etc. including some very mild ones, viz, nitrous acid (nitrites), ferric salts and cupric salts, which are without action on hydrobromic acid :

$$2HI+H_2O_2=2H_2O+I_2$$

$$2HI+O_3=O_2+H_2O+I_2$$

$$2HI+Cl_2=2HCl+I_2$$

$$2HI+Br_2=2HBr+I_2$$

$$2HI+2HNO_3=2NO_2+2H_2O+I_2$$

$$2HI+H_2SO_4=SO_2+2H_2O+I_2$$

$$2HI+2FeCl_3=2FeCl_2+2HCl+I_2$$

$$4HI+2CuSO_4=2H_2SO_4+Cu_2I_2+I_2$$

$$2HI+2HNO_2=2NO+2H_2O+I_2$$

$$5HI+HIO_3=3H_2O+3I_2$$

30·38. Tests : (i) HI or any metallic iodide when heated with conc. H_2SO_4 yields violet vapours of iodine.

(ii) On treatment with chlorine water, HI or a metallic iodide solution yields iodine which dissolves is CS_2 giving a violet solution. (iii) when $AgNO_3$ solution is added to HI or a metallic iodide solution, a yellow ppt. of AgI is formed which is insoluble in both HNO_3 and in ammonia.

30·39. Uses : Hydriodic acid is used in the laboratory as a reducing agent both for organic and inorganic reactions.

The iodides of metals are the salts of hydriodic acid and are prepared by neutralising hydriodic acid with an alkali. The iodides are all soluble in water with the exceptions of cuprous iodide, Cu_2I_2, silver iodide, AgI, lead iodide, PbI_2, mercurous iodide, Hg_2I_2 and mercuric iodide, HgI_2. Some of the iodides are used in medicine (KI), in photography (AgI).

30·40. Comparison of the Halogens :

The elements of the halogen family, viz., fluorine, chlorine, bromine and iodine, show striking similarities in their properties and behaviours. This justifies their inclusion in the same group (VII-B) of the periodic table. Their properties show a regular gradation with increasing atomic number from fluorine to iodine. Fluorine, the first member of the group, however, differs in some respcets, like its counterpsrt in other groups, from other halogens and resembles the neighbouring element oxygen of the previous group.

1. **Resemblances :—**

(a) None of them occur free in nature, they are found in the combined state.

(b) All of them are non-metals and highly electronegative elements.

(c) They are monovalent and form univalent anions in their halides e.g, NaF NaCl, NaBr and NaI.

(d) All the halogens give covalent diatomic molecules.

(e) The electronic arrangement in the outermost shell is the same in each case : F $-2s^2 2p^5$, Cl $-3s^2 3p^5$, Br $-4s^2 4p^5$, I $-5s^2 5p^5$.

(f) The halogens are all coloured due to absorption of visible light and possess bad smell.

(g) They all unite with hydrogen giving rise to acids. These hydracids fume strongly in moist air and are extremely soluble in water.

They all combine directly with metals and with phosphorus giving phosphorus halides.

(i) Except fluorine, all of them are obtainted by a similar process, e.g, by oxidising halides with MnO_2 and conc H_2SO_4.

2. Gradation in change of properties with the increase of atomic weight.

In this group, the intensity in any property always changes in the same way from fluorine to iodine. The gradual change in the physical and chemical properties of the halogen elements with the increase of their atomic weights, is evident from the following tables.

Physical properties of the halogens

Property	Fluorine	Chlorine	Bromine	Iodine
1. Atomic numbers	9	17	35	53
2. At. weight	19	35·45	79·9	126·9
3. Physical state at N. T. P.	Gas	Gas	Liquid	solid
4. Colour of the vapour	Pale yellow	Greenish-yellow	Red	violet
5. Odour	Peculiar irritating smell	Pungent and irritating smell	Smell like chlorine but more irritating to nose and throat	smell like chlorine and intensly irritating to eye and nose
6. Boiling pt. (°C)	– 187°	– 34°	59°	184°
7. Melting pt. (°C)	– 223°	– 102°	– 7°	114°
8. Density	1·108 (liquid at b. p)	1·557 (liquid at b.p.)	3·19 (liquid at 0°)	4·94 (solid)
9. Solubility in water	Decomposes water	fairly soluble	fairly soluble	very slightly solible
10. Electronegativity	4·0	3·0	2·8	2·5

Chemical proterties of the halogens

All the halogen elements are chemically very reactive but the reactivity decreases with increase in atomic weight.

Properties	Fluorine	Chlorine	Bromine	Iodine
1 Chemical activity	Most reactive, liberates Cl, Br and I from HCl, HBr and HI or their salts	Less reactive than F_2, liberats Br and I from HBr HI or their salts	Less reactive than chlorine, liberates Iodine from HI or its salts	Least reactive, cannot displace F, Cl, or Br from their hydroacids or salts
2. Reaction with : a) Hydrogen	Reacts explosively even in dark. Forms HF even at −25°	Combines on heating or in presence of sun light. Forms HCl	Forms HBr in contact with heated platinum	Slowly forms HI in contact with heated platinum
b) water	Decomposes water forming HF and ozonised oxygen	Dissolves to form chlorine water. which is decomposed in sunlight evovling oxygen	Dissolves to form bromine water slowly decomposed in sunlight setting free oxygen.	Slightly soluble, no action.
c) Metals	Almost all metals burn in the gas	Attacks all metals, many metals burn, e.g. Na.	Attack all metals, but a few burus e.g. K	Attacks all metals except platinum
d) Non-metals	Combines directly with all except N_2 & O_2	Combines directly with all, except C, N_2 & O_2.	Combines directly with all, except C, Si, N_2 and O_2	Combines directly with a few e.g. P, As, Sb.

Propertise	Fluorine	Chlorine	Brominee	Iodine
e) Alkalis i) cold ii) hot soln	At tacks water of the solution als ogives fluorides and F_2O	Forms chloride& hypochlorite Forms chloride and chlorate	Forms bromide &hypobromite Forms bromide and bromate	Forms iodide & hypoiodite Forms iodide and iodate
f) oxidising action	Vigorous oxidant	Stong oxidising agent	oxidising power is less than Cl_2 but more than I_2	Mild oxidising agent
g) Bleaching action	Destroys the material	Readily bleaches in presence of moisture	Slowly bleachesin presence of moisture	No bleaching action
h) Starch solution	Attacks water of the solution	No change of colour	Solution is coloured orange yellow	Solution is coloured blue
3. Action of oxidants, O_2 etc.	The oxides F_2O to F_2O_2 are known	Indirectly forms Cl_2O, ClO_2, Cl_2O_5 and Cl_2O_7	Oxidised to BrO_3 by O_3 Indirectly forms Br_2O & BrO_2	oxidised to iodic acid by O_3 and HNO_3 Forms I_2O_4 I_2O_5 & I_4O_9

These similarties in behaviour and gradation in properties are also extended to their hydracids (HF, HCl, HBr and HI). This is evident from the following table.

The properties of the halogen hydracids.

Properties	HF	HCl	HBr	HI
1. Physical state at 15°C	Colourless liquid	Colourless gas	Colourless gas	Colourless gas
2. Melting pt, °C	−83·7°	−114°	−87°	−51°
3. Boiling pt, °C	19·5°	−85°	−67°	−36°
4. Solubility in water	Miscible with water	Highly soluble	Highly soluble	Highly soluble
5. In moist air	Fumes in moist air	Fumes in moist air	Fumes in moist air	Fumes in moist air
6. Stability	Very stable	Stable, dissociates at 1500°C	dissociates at 800°C	dissociates at 180°C
7. Strength of acid	aqueous solution is weak acid forms acid salts	Solution is strong monobasic acid	Solution is strong monobasic acid	Solution is strong monobasic acid.
8. Action of oxidants				
a) KMnO$_4$ ANO$_3$ and MnO$_2$	No action	oxidised to chlorine	oxidised to bromine	oxidised to iodine
b) H$_2$O$_2$, Cl and H$_2$O$_2$	"	"	"	"
c) Cu^{2+}, Fe^{3+} ion HNO^2	"	"	No action	"

Exercise 30

1. How was fluorine isolated ? Why could not Fluorine be prepared by the same method as in the case of chlorine ? In what way is it exceptional among the halogens ?

2. Describe, with a heat sketch, how you would prepare a sample of chlorine free from hydrogen chloride. Suggest a method for ready supply of chlorine in the laboratory.

3. Explain, with equations, the action of chlorine upon (i) ammonia, (ii) hydrogen sulphide, (iii) water, (iv) potassium iodide, (v) Calcium hydroxide, (vi) sulphurous acid, (vii) molten tin, (viii) carbonmonoxide and (ix) mercury.

4. Describe and explain three typical reactions in which chlorine gas acts as an oxidising agent. Discuss the bleaching property of chlorine, and mention its more important uses.

5. What is the chief source of bromine and how is it obtained in the pure state ? How may (a) hydrogen bromide, (b) potassium bromide be prepared from bromine ? Discuss the reactions of bromine with (i) potassium iodide, (ii) phosphorus, (iii) sulphur dioxide, (iii) sodium carbonate.

6. What are the chief sources of iodine ? How is iodine prepared on a large scale ? How is iodine purified ? In that ways and under what conditions would iodine react with the following ? (i) KOH, (ii) $KClO_3$, (iii) H_2S. (iv) SO_2, (vi) HNO_3, (vii) Sodium thiosulphate, (vii) potasium iodide.

7. Give illustrations to show that the chemical activity of the halogens increases successively from iodine to fluorine.

8. What are halogens ? Why are they so called ? Give in a tabular form the physical and chemical properties of halogens to illustrate gradation of their properties.

9. How is hydrocloric acid obtained commercially and for what purposes is it used ? How would you establish that its formula is HCl ? How would you detect traces of chlorine in HCl ?

10. How and under what conditions hydrochloric acid reacts with (a) iron, (b) tin, (c) Aluminium, (d) copper, (e) potassium iodide (f) nitric acid, Give equations.

11. How is anhydrous hydrofluoric acid prepared ? What kind of vessels are used in the experiment ? What happens when an aqueous solution of hydrofluoric acid is electrolysed ? What is meant by etching of glass ?

12. How would you prepare (a) hydrogen chloride and (b) hydrogen iodide in the laboratory ? Why different methods are employed in the two cases ?

13- How would you prepare a sample of aqueous HBr ? How is hydrobromic acid distinguished from hydriodic acid ? Why hydriodic acid behaves as a reducing agent ?

14. Compare and contrast the properties of the hydracids of the halogens.

15. How do you distinguish between :

(a) Grey solid iodine and graphite,

(b) Solid sample of potassium bromide and iodide,

(c) Powdered MnO_2 and charcoal,

(d) Potassium chloride and potassium chlorate solution.

16. (a) How do you prove the presence of chlorine in potassium chlorate ?

(b) How would you remove a trace of chlorine present in oxygen ?

(c) Compare the action of Conc H_2SO_4 on sodium chloride, sodium bromide and sodium iodide.

(d) Explain the behaviour of MnO_2 when it is heated with HCl acid and when it is heated with potassium chlorate,

(e) Electrolysis of fused common salt liberates sodium metal at the cathode, but electrolysis of brine gives hydrogen and sodium hydroxide. Give reasons for this difference.

17. Describe what happens when :

(a) A crystal of iodine is heated in flask,

(b) A mixture of KI and KIO_3 is acidified,

(c) Chlorine water is added to potassium iodide solution, and then shaken with carbon disulphide,,

(d)- Chlorine acts on a suspension of iodine in water

(e) Silver nitrate solution is added to HCl and then excess of ammonia is added.

(f) Conc. hydrochloric acid is added to bleaching powder.

18. Arrange the halogens in terms of their oxidising power, and the hydrogen halides in terms of their reducing power. Give reasons and evidences for the arrangement you made.

1982

CHEMISTRY

First Paper

Group A

Answer Question 1 and any Three from the rest

1. (a) Equal masses of two gases A and B are kept in two separate vessels at the same temperature and pressure. If the ratio of the molecular weights of A and B 2 : 3 and the ratio of the volumes of the two vessels.

(b) What volume of carbon dioxide gas at standard temperature and pressure may be obtained from one kilogram of calcium carbonate ? [Ca = 40].

Or, (a) 1 litre of a gaseous element reacts with 2 litres of another gaseous element to form 1 litre of a gaseous compound (all the volumes being measured at the same temperature and pressure). Both the elements are known to be diatomic. Taking the symbols for the two elements as X and Y respectively, find the molecular formula of the compound.

(b) If the volume per gram of a gas be 280 millilitres at the standard temperature and pressure, what is its molecular weight ?

2. Explain what is meant by the 'partial pressure' of a gas and state Dalton's law of partial pressures.

A mixture containing 2·0 gm hydrogen and 8·0 gm oxygen is kept at 27°C in a vessel whose volume is 20·0 litres. What is the total pressure inside the vessel ?

3. (a) State Dulong and Petit's law.

(b) 1·020 gm of a metallic oxide contains 0·540 gm of the metal. Calculate the equivalent weight of the metal and hence its atomic weight with the help of Dulong and Petit's law. Taking the symbol for the metal as M, find the molecular formula of the oxide. [Specific heat of the metal is 0·216 calorie per degree per gram].

4. (a) Explain the difference between 'normal' and 'standard' solutions of an acid.

(b) If 40·0 millilitres of a sulphuric acid solution be required for titrating 2·65 gm of sodium carbonate dissolved in water, using methyl orange as the indicator, what is the normality of the acid ? [Na = 23].

Explain whether there would have been any difference, if phenophthalein, instead of methyl orange, were used as the indicator.

5. (a) Explain the electronic concept of oxidation and reduction with suitable examples and show that oxidation and reduction occur simultaneously.

(b) Explain with suitable examples that the oxidation number of the same element may be positive in one of its compounds and negative in another.

(c) Complete the following equation with the help of oxidation number :

$$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

6. Explain what is meant by the state of equilibrium of a chemical reaction.

Write the expression for the 'equilibrium constant' for the undermentioned reaction.

$$2M\ (gas) + N\ (gas) \rightarrow 2P\ \ (gas)$$

Suppose that the above reaction is endothermic, and that at a definite temperature and pressure M, N and P are in equilibrium in a closed vessel. Now, (i) if the volume of the vessel be increased, keeping the temperature unchanged will the amount of P increase or decrease ? (ii) If the temperature be increased, keeping the volume unchanged will the amount of P increase or decrease ?

Give reasons for your answer in each case.

Group B

Answer Question 7 and any Three from the rest.

7. State with reasons whether you expect the reactions to occur as shown below :

(i) $Fe + HCl\ (dilute) \longrightarrow FeCl_3 + H_2$.
(ii) $Cu + H_2SO_4\ (dilute) \longrightarrow CuSO_4 + H_2$.
(iii) $K_2SO_4 + HNO_3$ (concentrated)
$+ heat$
$\longrightarrow KNO_3 + H_2SO_4$.

Or,

(a) State with reasons whether concentrated sulphuric acid and quicklime are suitable or unsuitable for drying hydrogen iodide and ammonia.

(b) Name any two good drying agents other than the two mentioned above.

8. (a) Under what conditions does water react with (i) iron and (ii) coke and what are the products ? Give equations.

(b) Explain whether a dilute aqueous solution of magnesium sulphate will behave as 'hard water'.

9. (a) Explain, with a sketch, how Kipp's apparatus can be used for a ready supply of hydrogen sulphide whenever required in the laboratory.

(b) State and explain what happens when hydrogen sulphide is passed into a solution containing both $CuCl_2$ and $ZnCl_2$, acidified with dilute hydrochloric acid.

10. (a) What is 'superphosphate of lime' ? How is it prepared ?

(b) State with equations what happens when :—

(i) White phosphorus is heated with a concentrated solution of potassium hydroxide.

(ii) Water is slowly added to a mixture of red phosphorus and iodine.

(c) How can white phosphorus be converted into red phosphorus ?

11. (a) Explain the follwing phenomena :—

(i) Moist chlorine is a strong bleaching agent. but it cannot bleach the marking made with an ordinary pencil ;

(ii) Iodine is sparingly soluble in water, but its solubility is much higher in a solution of potassium iodine.

(b) State with equations how you will prepare : 3½+2½

(i) nitric acid from ammonia and

(ii) ammonia from nitric acid.

12. State with equations what happens when (any *four*) :—

2½×4

(i) Ozone is allowed to react with ethylene.

(ii) A mixtune of gaseous carbon dioxide and ammonia is heated under high pressure.

(iii) A burning magnesium wire is inserted into a jar of carbon dioxide.

(iv) A mixture of ammonium chloride and sodium nitrite solutions is heated.

(v) Nitrogen gas is passed over heated metallic calcium.

CHEMISTRY—1982

2nd Paper

Group A

Answer any two questions

I. (a) Name two radioactive elements. Complete the following radioactive transformations mentioning the mass number and atomic number of each product :

$$ {}^{238}_{92}A \xrightarrow{\text{—one } \alpha \text{ particle}} B $$

$$ {}^{210}_{82}C \xrightarrow{\text{—one } \beta \text{ particle}} D $$

(b) What are the differences between a radioactive change and a chemical change? State why some elements are radioactive whereas others like Gold (Au) are not so.

3. (a) What do you understand by the statement 'Solubility of potassium nitrate at 20°C is 31'? State what information can be obtained by a Solubility curve.

(b) 300 gms. of a staturated solution of potassium nitrate at 100°C is cooled to 10°C. Calculate the weight of the salt that crystallises out of the solution. (The solubility of KNO_3 at 10°C and 100°C are 20 and 250 respectively.)

(c) Of the two compounds, ethyl alcohol and diethyl ether, ethyl alcohol has a much higher boiling point. How would you account for it?

3. (a) State the Periodic Law in terms of atomic numbers. State what a particular period in the Periodic Table represent.

(b) From their position in the Periodic Table name (i) the most electronegative element in the halogen family, (ii) the element of the pair S_{16} and Cl_{17} which is more electropositive.

(c) State why the isotopes of an element have similar chemical properties. The mass numbers of two isotopes of an element are 35 and 37. They are present in the proportion of 75 and 25 per cents respectively. Calculate the atomic weight of the element.

4. (a) What do you understand by 'Electro Chemical Equivalent' and 'Faraday' ?

(b) Calculate the values of (i) Faraday, (ii) Electro Chemical Equivalent of Silver and (iii) the charge of an electron from the following data :

A current of 6 amperes is passed through a $AgNO_2$ solution for 10 minutes when 4·029 gms of silver is obtained.

(Given :—the atomic weight of $Ag = 108$)

Group B—Answer any two questions

5. (a) Furnish the following informations for the extraction of aluminium from alumina by the electrolytic reduction process—

(i) composition of the materials used as electrolyte.

(ii) electrode reactions (iii) electrolytic material in the electrolytic cell consumed. (iv) collection of the metal.

(b) Name the materials charged in the Blast Furnace for the production of cast iron. What role do the materials other than the iron ore, play in the extraction process ? Explain with equations.

6. (a) Write a short technical note on any one of the following :—

(i) Quick lime. (ii) Bleaching powder. (iii) Caustic soda.

(b) State what happens when (attempt any three) :

(i) a mixture of ferric oxide and metallic aluminium is strongly heated.

(ii) iron powder is added to a copper sulphate solution.

(iii) a piece of metallic sodium is dropped into water.

(iv) a piece of burning magnesium ribbon is inserted in a jar of nitrogen.

(In each case name the products and give equations.)

7. (a) The eletropositive character of the elements is in the following order :

$Na > Mg > Al > Zn > Fe > H > Cu > Pt.$

From the above, answer the following questsons :

(i) Which one of Mg and Fe has higher oxidising power ?

(ii) Which one of Cu and Zn can be liberated from its sulphate solution by adding the other metal ?

(iii) Which one of Na and Cu is expected to occur in the free sate in nature ?

(iv) Which one of Mg and Fe you will select for extraction by the electrolytic reduction process ?

(v) Which one of Na and Fe is not expected to be extracted by the carbon reduction process ?

(b) State the principle underlying the manufacture of soda ash by the Solvay process. Give equations for the reactions.

Group C—Attempt any three questions

8. (a) Write the structural formulas of the following pairs of compounds :

But-1-ene and But-2-ene.

But-1-yne and But-2-yne.

(b) A hydrocarbon contaning two carbon atoms decolorises bromine water and is hydrolysed by H_2SO_4 in the presence of $HgSO_4$ to form a compound which on heating with bleaching powder produces choloroform.

Name the hydrocarbon and give questions in support of your statement.

(c) How is the hydrocarbon prepared in the laboratory ?

9. State how the following compounds are prepared starting from benzene (mention only the coditions and give equations) :—
(a) Toluene. (b) Benzoic acid. Aniline. (d) Phenol, (e) Benzyl Chloride.

10. State one chemical in each case by which you can distinguish between the following pairs of compounds : (a) Nitrobenzene and aniline. (b) Acetone and acetaldehyde. (c) Ethyl alcohol and methyl alcohol. (d) Ethyl acetate and diethyl ether. (e) Formic acid and formaldehyde.

11. (a) Describe the preparation of acetyl chloride in the laboratory. How is it purified ?

(b) Starting from acetyl chloride how would you prepare the following compounds ? (The reactions and conditions are to be mentioned) :

(i) Acetic anhydride. (ii) Acetamide. (iii) Ethyl acetate.

12. Name the principal organic products (A—J) in the following reactions :

CHEMISTRY—1983

First Paper

Group—A

(Answer Question 1 and *any three* from the rest)

1. (a) Is the number of molecules in one mole of a gas at 100°C and 300 mm pressure equal to, greater than or less than Avogadro number ? 1

(p) A mixture of hydrogen and oxygen contains 20% by weight of hydrogen. What is the total number of molecules present per gram of the mixture ? 4

Or

(a) Two metals A and B have the same equivalent weight, but the atomic weight of B is twice that of A. How can it be explained ? 1

(b) If the equivalent weight of a metal (M) be x, and the formula of its oxide be $M_m O_n$, show that the atomic weight of

$$M = \frac{2xn}{m}$$ 4

2. State the law of 'reciprocal proportions' for chemical combination. 3

A, B and C are three elements. 1 g A combines with 1·33 g B; 1 g B combines with 0·125 g C; 1 g C combines with 6·00 g A. Show whether these results are in agreement with the law of reciprocal proportions. 3

Explain this law with the help of atomic theory. 4

3. (a) What is meant by 'vapour density'? Establish the relation between vapour density and molecular weight. 1+2

(b) What is 'empirical formula'? How can the molecular formula of a gaseous compound be obtained from its empirical formula? 1+1

(c) 60 ml of a mixture of CO and H_2 was mixed with 40 ml oxygen and exploded in a eudiometer. After cooling, the volume was found to be 30 ml. Find the composition of the original mixture. [Volumes were measured at the same pressure and temperature].

4. (a) Find the value of the 'gas constant' R in any unit. 3

(b) Find the volume of 2·2 g carbon dioxide at 27°C and 570 mm pressure. 4

(c) State Graham's law of diffusion with one example. 3

5. (a) Explain with one example what is meant by an amphoteric oxide.

(b) Explain why an aqueous solution of ammonium chloride is acidic. 3

(c) 100 ml of a solution of calcium hydroxide required 20 ml of a 0·030 N HCl solution for neutralisation. Find the normality of the alkali solution. How many grams of calcium hydroxide are present per litre of this solution? [Ca=40] 2+2

6. (a) Explain whether the two reactions, stated below, are oxidation-reduction reactions: 2+2

(i) $Mg+H_2SO_4=MgSO_4+H_2$

(ii) $MgO+H_2SO_4=MgSO_4+H_2O$.

(b) Explain the significance of the relative positions of hydrogen, iron and copper in the elctropotential series. 3

(c) Write the expression for the equilibrium constant (K) for the reaction.

$$N_2\ (gas) + 3H_2\ (gas) \rightleftharpoons 2NH_3\ (gas).$$

State, giving reason, whether the value of K will change, if excess nitrogen is used in this reaction. 1+2

Or,

(a) Describe how the equivalent weight of Copper can be determined. 5

(b) 0·20 g of Mg was completely dissolved in a dilute H_2SO_4 acid solution. At the end of the reaction the volume of dry Hydrogen gas collected was found to be 185·0 millilitres at N.T.P. Calculate the eqivalent of Magnesium. 4

(c) What more data is necessary in order to find out the atomic weight of Magnesium ? 1

Group B

(Answer Question 7 and any three from the rest)

7. Answer the following questions, giving reasons :—

(a) Will you use HCl or HNO_3 for preparing H_2S from FeS ? 2

(b) Will you use HCl or H_2SO_4 for preparing CO_2 from marble ? $1\frac{1}{2}$

(c) Will you use CaO or $CaCl_2$ for drying SO_2 gas ? $1\frac{1}{2}$

Or,

(a) A bottle contains a powdered salt which may be KCl, KBr or KI. You have conc. H_2SO_4, test tubes and a Bunsen burner. Using only these, how will you identify the salt ? 3

(b) How will you separate the two ingredients from a powdered mixture of potassium iodide and iodine ? 2

8. (a) Describe an experiment to show that nascent hydrogen is a stronger reducing agent than ordinary hydrogen. 3

(b) Name an element which can liberate hydrogen from cold water, and show the reaction that occurs. 2

(c) What happens when chlorine water, is exposed to bright sunlight ? 2

(d) Why is hard water unsuitable for use in boilers ? 1

(e) What reaction does occur between hydrogen peroxide and ozone ? 2

9. (a) Under what conditions does carbon monoxide react with (i) caustic soda and (ii) water ; and what are the products ? Give equations. 3×2

(b) How can small amounts of CO in air be detected ? $1\frac{1}{2}$

(c) How can CO be removed from a mixture of CO and CO_2 ? $1\frac{1}{2}$

(d) Name the two principal ingredients of coal gas. 1

Or,

(a) Describe how pure chlorine gas is prepared in the laboratory. 6

(b) State what happens when with equations :—

(i) Chlorine gas is passed through a solution of SO_2.

(ii) Starch-Iodide paper is held in a jar of chlorine gas. 2+2

10. (a) State and explain the conditions required for the industrial production of SO_3 from SO_2. 6

(b) Briefly describe the process of preparation of phosphorus from bone ash. 4

11. (a) How will you prove that nitric acid contains oxygen ? 3

(b) What happens when ammonia gas is passed over (i) heated cupric oxide and (ii) heated metallic sodium separately ? Give equation in both cases. 2×2

(c) What happens when ammonium nitrate is heated ? Give equation. 2

(d) Cite a reaction to show that phosphine is basic. 1

12. State with equations what happens when (any *four*) : $2\frac{1}{2}\times 4$

(a) Ammonia and carbon dioxide are passed into a suspension of gypsum and water.

(b) Hydrogen peroxide is added to a solution of potassium permanganate acidified with dilute sulphuric acid.

(c) A mixture of sand and sodium carbonate is fused by heating.

(d) Potassium nitrite is added to a solution of potassium iodide acidified with dliute sulphuric acid.

(e) Phosphine is passed through an acidified solution of cupric sulphate.

(f) Solid Iodine is added to a solution of Potassium Iodide.

CHEMISTRY—1983

2nd Paper

Group A

(Answer any Two questions)

1. (a) What is understood by the electronegativity of an element ? How are the valency and electronegativity of an element related to its position in the Periodic Table ? 4

(b) The densities in g/cm^3 of the Group IA metals in the Periodic Table are : Li = 0·534 ; Na = 0·971 ; K = 0·862 ; Rb = 1·532 ; Cs = 1·900. Calculate the atomic volumes of these metals and decide whether density or atomic volume shows a greater regularity in the Periodic Law.

(Li = 7 ; Na = 23 ; K = 39 ; Rb = 85·5 ; Cs = 133). 4

(c) What are the defects of the Mendeleeff's Periodic Table ?

Or,

(a) Define 'Isotope' with one example.

(b) Justify with reasons the statement :—

'The position of Hydrogen is not fixed in the Periodic Table'. 3

(c) A radioactive element $_zX^A$ loses first an α-particle and and then one β-particle. What would be the mass number and atomic number of the resulting new element ? 2

(d) What change is observed in the gas when a stream of α-particle is passed through it ? From which part of the atom β-particles are ejected in a radioactive emission ? What is the resultant element formed when a radioactive element becomes completely inactive ? 3

2. (a) Elements A, B and C have atomic number 17, 18 and 20 respectively.

(i) Write down the arrangements of the electrons in A, B and C.

(ii) Of A, B and C, which is a metal and which is a non-metal ?

(iii) Write down the formula of the compound formed in between A and C.

(iv) Which type of bonding is expected in the compound formed in between A and C ? Justify your answer. 5

(b) What is meant by an ionic bond ? What are its characteristics ? How does it differ from covalent bond ? 5

3. (a) Account for the following :

(i) Sulphur and oxygen belong to the same group in the Periodic Table. but the hydride of the former is a gas whereas that of the latter is a liquid.

(ii) Of carbon dioxide and sulphur dioxide, the former has no dipole moment whereas the later has dipole moment.

(iii) The mass number and atomic weight of an element are not always the same. 2 × 3

(b) Write short notes on :—(i) Solubility product. (ii) Dialysis. 2 × 2

4. (a) State the two laws of electrolysis of Faraday. 4

(b) A current of 1·50 amperes at a potential of 6 volts is passed through a 4·0 litre of one molar Copper sulphate solution in between two Platinum electrodes for two hours. Calculate the masses of electrolytic products at the two electrodes. [Cu = 63·5] 4

(c) What happens when a crystal of 'hypo' is added to a supersaturated solution of it ? 2

Group B

(Answer *any two* questions)

5. In connection with the extraction of sodium by electrolysis of sodium chloride, furnish the following informations :

(i) Composition of the electrolyte. 1

(ii) Electrode reactions and nature of electrodes. 2

(iii) Collection of the metal. 1

(iv) What happens if the same reaction is carried out in aqueous solution of sodium chloride ? 2

(b) Name a metal which can be extracted by the carbon reduction process. Give equations of all the chemical reactions necessary for the extraction of the metal from its ores. 1+3

6. (a) State with equations what happens when (attempt any three) :—

(i) a piece of aluminium foil is dipped into copper sulphate soultion.

(i) sodium carbonate solution is added to a solution of ferric chloride.

(iii) crystaline ferrous sulphate is strongly heated.

(iv) KI solution is added in excess to a solution of $CuSO_4$. 6

(b) How are the following compounds prepared ?

(answer any two) :—

(i) Cuprous chloride from copper carbonate.

(ii) Plaster of Paris.

(iii) Sodium carbonate. 4

7. Account for the following :—

(a) When H_2S is passed through a solution containing Copper Sulphate and Zinc Sulpate acidified with dil HCl, Cu^{++} is precipitated but not Zn^{++}. 3

(b) Aluminium cannot be extracted from alumina by the carbon reduction process. 2

(c) A piece of Iron becomes passive when dipped into conc. HNO_3.

(d) Anhydrous Magnesium Chloride cannot be prepared by heating hydrated Magnesium Chloride. 3

Or, Write notes on :

(a) Manufacture of steel by open hearth process. 3

(b) Thermite process. 2

(c) Purification of Bauxite for the extraction of Alumininm. 3

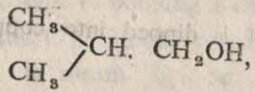
(d) Galvanisation and its utility. 2

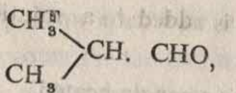
Group C

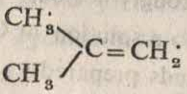
(Answer any three questions)

8. (a) How are the valency bonds of carbon distributed in space in the molecules of Methane, Ethylene and Acetylene ? How can you test for unsaturation in an organic compound ? 5

(b) Name the following compounds according to the IUPAC nomenclature :—

(i)

$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.\ CH_2OH,$

(ii)

$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.\ CHO,$

(iii)

$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CH_2;$

3

(c) Write down the structural formulae of the following :

(i) But-1-yne.

(ii) But-1, 3-diene. 2

9. (a) Name the reagents necessary for the following transformations :

(i) Acetone ⟶ Diacetone alcohol.

(ii) Acetamide ⟶ Methyl amine.

(iii) Acetone ⟶ Chloroform.

(iv) Acetic anhydride ⟶ Ethyl acetate.

(v) Formaldehyde ⟶ Urotropine.

(vi) Acetonitrile ⟶ Acetic acid. 6

(b) State one chemical reaction in each case by which you can distinguish between the following pairs of organic compounds :

(i) Formic acid and acetic acid.

(ii) Diethyl ether and ethyl alcohol. 4

10. (a) How would you prepare pure aniline from nitrobenzene ? 6

(b) State with equations the reactions of aniline with the following reagents :

(i) acetic anhydride,

(ii) bromine water. 4

11. (a) An organic compound A of molecular formula C_7H_8 on saturation with excess of chlorine in the presence of sunlight gives another compound B of molecular formula $C_7H_5Cl_3$ which on hydrolysis by lime water under pressure gives another compound C of molecular formula $C_7H_6O_2$. The compound C can also be obtained from A by oxidation by $K_2CrO_2O_7 + H_2SO_4$. What are the compounds A, B and C ? Explain the reactions.

(b) How would you synthesise the compound A ? 2

(c) What happens when chlorine gas is passed through A in the presence of iron powder ? 2

12. How would you prepare the following compounds as directed ?—

(a) Phenol from benzene.

(b) Acetic acid from acetylene.

(c) Diethyl ether from Ethyl alcohol.

(d) Chlorobenzene from aniline. $2\frac{1}{2} \times 4$

CHEMISTRY—1984

First Paper

Group 'A'

Answer Question 1 and any *Three* from the rest.

1. (a) How will completely separate the individual constituents of a mixture consisting of Common Salt, Ammonium chloride and Sand ?

(b) Calculate the weight of one Magnesium atom. (Mg = 24)
4 + 1 = 5

Or,

(a) 24 gms. of solid element require 44·8 litres of Oxygen at N. T. P. for its complete conversion into a gaseous oxide. The gaseous oxide occupies a volume of 44·8 litres at N. T. P. What is the weight in gms. of the gaseous oxide produced and what is its vapour density ?

(b) Calculate the number of molecules of water present in 1·8 c.c of water at 4°C. $3+2=5$

2. (a) State Gay-Lussac's Law of Gaseous Volume.

(b) Show the nature of graph that would be obtained when the volume of a given mass of a gas at constant presure is plotted against the temperature on the Centigrade Scale. Indicate the point on this graph which corresponds to the zero of the Absolute Scale of temperature.

(c) $PV=RT$. State why this equation is called the molar gas equation. Write the individual values at the standard condition of P, V and T of the gas equation $PV=RT$ in the C.G.S. units and hence calculate the value of the Molar Gas Constant in the C.G.S. unit.

(d) 112·0 gms. of pure Iron are completely converted into Ferric chloride and dissolved in water. How many litres of H_2S gas at N.T.P. will be required to convert this entire amount of Ferric chloride into Ferrous chloride? [Fe=56, Cl=35·5]

$2+2+4+2=10$

3. (a) State the Law of Multiple Proportions for chemical combination. Give one example to illustrate it.

(b) Two oxides of a metal M were separately heated to constant weight in a current of Hydrogen. water formed was collected and weighed separately in two cases. The following results were obtained :

(i) 0·795 gm. of first oxide yielded 0·18. gm. of water.

(ii) 2·86 gm. of second oxide yielded 0·36 gm. of water.

Show that these results are in agreement with the Law of Multiple Proportions.

$4+6=10$

4. (a) Define—Standard solution and Normal solution.

(b) An aqueous solution is prepared by dissolving 40 gms. of NaOH in 1000 c.c. water. State with reasons whether this solution can be called a normal solution or not.

(c) 5·35 gm. of an impure sample of NH_4Cl is strongly heated with excess concentrated solution of caustic soda until all ammonia is given off. The resultant ammonia is completely absorbed in 120 c.c. of N H_2SO_4 solution which further required 60 c.c. of 0·5 N NaOH solution for complete neutralisation. Calculate the percentage of pure NH_4Cl in the sample. [N = 14, Cl = 35·5]

2+2+6=10

(5). (a) What information is obtained from the following equation :

$Zn + H_2SO_4 = ZnSO_4 + H_2$

(b) Write down the limitations of chemical equation.

(c) A monobasic acid containing Nitrogen, Hydrogen and Oxygen only gave the following percentage composition by weight.

N—22·2%, H—1·59%.

Calculate the molecular formula of the acid. [N = 14]

4+2+4=10

6. (a) Find out the oxidation numbers of carbon in Methane and Carbon dioxide.

(b) Balance the following chemical equation by oxidation number method.

$C + H_2SO_4 \rightarrow CO_2 + SO_2 + H_2O$

(c) Why a chemical equilibrium is called a dynamic equilibrium ?

(d) The chloride of a metal *M* contains 30% by weight of chlorine and is isomorphus with Potassium chloride (KCl). Calculate the atomic weight of M.

(Atomic weight of chlorine = 35·5) 2+2+2+4=10

Group B

Answer Question 7 and any *Three* from the rest.

7. (a) Name one drying agent and cite one example of its application.

(b) Name two bleaching agents and explain how they function.

(c) How hardness of water is expressed ?

(d) What is Aqua regia ? 1+2+1+1=5

8. (a) Describe how Sulphur dioxide gas is prepared in the laboratory.

(b) Describe what happens when H_2S gas is passed separately through.

(i) a suspension of Iodine in water, and (ii) an acidified solution of Potassium dichromate solution.

Give equations in both cases. 6+2×2=10

9. In the Haber's process of manufacture of Ammonia the following reaction is used :

$N_2+3H_2 \rightleftharpoons 2NH_3+24000$ Cal. (Heat)

(a) What pressure and temperature are maintained tn the Haber's process for manufacture of Ammonia ? What catalyst and promoter are used ?

(b) Explain the justification of using the above-mentioned pressure and temperature.

(c) State the sources of Nitrogen and Hydrogen.

(d) State what happens with balanced equations when ammonia gas is passed separately through.

(i) $CuCo_4$ solution, and (ii) $FeCl_3$ solution.

2+3+1+2×2=10

10. A soft white metal *A* (Atomic no. 11) When added to water produces a compound *B* soluble in water and a gas *C*. The gas *C* when passed over heated cupric oxide produces copper and water. The aqueous solution of *B* when added to an aqueous solution of Zinc sulphate produces a compound. *D* which is precipitated. *D* becomes completely soluble when excess solution of *B* is added to it.

(ii) Indentify *A*, *B*, *C* and *D* (give the names only).

(ii) Describe the chemical reactions that occur in the above mentioned for stages and give equations in all cases. 2+8=10

11. Explain why :

(i) Silent electric discharge is passed in the preparation of Ozone from Oxygen.

(ii) Most of the metals do not liberate hydrogen on reaction with Nitric acid.

(ii) SO_3 gas is not absorbed in water but instead absorbed in 98% H_2SO_4 acid during the manufacture of H_2SO_4 acid.

(iv) Phenolphthalein is not used as an indicator in the titration of an aqueous solution of Na_2CO_3 by an aqueous solution of HCl.

(v) In the laboratory method of preparation of PH_3, the air inside the flash (in which PH_3 is prepared) is replaced by coal gas.

2 × 5 = 10

12. State with equations what happens when :

(Answer any *five*)

(a) Iron powder is added to an aqueous solution of Ferric chloride solution containing hydrochloric acid.

(b) Sulphur powder is heated with excess of concentrated solution of Caustic Soda.

(c) Ozone gas is passed through Stannous chloride solution containing hydrochloric acid.

(d) Conc. H_2SO_4 acid is allowed to fall drop by drop over red hot pumice stone.

(e) Hydrogen sulphide gas is passed through concentrated Sulphuric acid.

(f) Manganese dioxide powder is heated strongly with concentrated Hydrchloric acid.

2 × 5 = 10

CHEMISTRY—1984

2nd Paper

Group 'A'

(Answer any two Questions)

1. (a) Define 'Atomic Weight' and 'Mass Number' of an element.

(b) Explain why the atomic weight of chlorine is fractional.

(c) Atomic weight of an element is 207. It has two isotopes of Mass Numbers 206 and 208. Calculate the percentage of atoms having Mass Number 208 present in the element.

(d) 'Most of the space inside an atom is empty, the nucleus occupies an insignificant space in the atom and it is the nucleus which is the seat of positive charge. Describe how-Rutherford established these facts.

(e) A radioactive element $_{89}X^{227}$ undergoes a series of radioactive disintegrations involving loss of several alpha and beta particles producing finally the non-radioactive $_{82}Z^{207}$ Calculate separately the total numbers of alpha and beta particles expelled in the entire process. $5 \times 2 = 10$

2. (a) Define 'water of crystallisation'.

(b) Crystals of Na_2CO_3 $10H_2O$ when exposed to air lose a part of this water to be converted to Na_2CO_3. H_2O. Give the general name of such phenomenon and explain the mechanism of the process.

(c) Show the distribution of electrons in three elements *A*, *B* and *C* having atomic numbers 9, 13 and 17 respectively. State which one above three elements is the most electropositive and which one is the most electronegative.

(d) 50 gms. of a saturated aqueous solution of KNO_3 at 25°C contains 21 gms. of the salt. Calculate the solubility of KNO_3 at 25°C. $1+3+4+2=10$

3. (a) Give reasons :

(i) H_2S can precipitate CuS but not ZnS when passed through an acidfied solution containing copper salt and zinc salt.

(ii) Anhydrous liquid hydrogen chloride is non-conductor of electricity but its aqueous solution is an electrolyte.

(b) Explain how a colloidal solution differs from a true solution.

(c) 1 gm. of hydrated crystalline copper sulphate gave on heating 0·6393 gms. of the anhydrous salt. Calculate the number of molecules of water of crystallisation per molecule of the hydrated salt. [Cu=63·5, S=32, O=16] $2 \times 2+3+3=10$

4. (a) State Faraday's laws of electrolysis.

(b) Calculate the quantity of electricity required to liberate one gram equivalent of Hydrogen, given that Electrochemical equivalent of Hydrogen is 0·0000104 gm./coulomb. How much amount of silver will be liberated if this quantity of electricity is passed through a $AgNO_3$ solution ? (Ag=108)

(c) The quantity of electricity necessary for liberating one gram equivalent of Hydrogen is equal to the total charge carried by one gram equivalent of hydrogen ion in solution. Hence calculate the charge carried by a hydrogen ion.

(d) Same quantity of electricity is passed through acidulated water and through the aqueous solution of the chloride of a metal *X* when in the first case 7·4 litres of hydrogen at S.T.P. and in the second case 21 gm. of the metal are deposited. Calculate the chemical equivalent weight of the metal. 4+2+2+2=10

Group 'B'

(Answer any *two* questions)

5. (a) Briefly describe the principles of extraction of metals by the following processes and give an example of each :

(i) Carbon reduction process

(ii) Electrolytic reduction process

(iii) Self reduction process.

(b) Name an alloy with its constituents. 3 × 3 + 1 = 10

6. In connection with the extraction of cast iron from haematite with the help of blast furnace, furnish the following information :

(i) basic raw materials used in the process

(ii) role of each raw material in the process of extraction

(iii) role of air used in the process

(iv) reactions in the blast furnace leading to formation of Iron

(v) collection of the metal after formation

(vi) two by-products and their uses. 1+3+1+2+1+2=10

7. State with equations what happens when—(*any five*)

(a) Steam is passed over red hot iron filings.

(b) SO_2 gas is passed first slowly and then in excess through lime water.

(c) An iron knife is dipped into copper sulphate solution,

(d) H_2S gas is led into ferric chloride solution.

(e) Solid sodium bicarbonate is heated.

(f) Ferrous sulphate is strongly heated. 2 × 5 = 10

Group 'C'

(Answer any *three* questions)

8. (a) What are the values of the

Hydrogen—Carbon—Carbon angles in ethane, ethylene and acetylene ?

(b) Write the structural formulae of the following compounds and name them according to I.U.P.A.C. system of momenclature :

(i) Tertiary butyl alcohol.
(ii) Isobutane.

(c) Mention two chemical reactions with equations wihch exhibit the properties of alcoholic hydroxyl group of an organic compound. $3+4+3=10$

9. (a) An organic compound containing carbon, hydrgen and oxygen on analysis is found to contain 65% carbon and 13·5% hydrogen. 0·185 g of this compound, when vaporised occupies 56 c.c. at S.T.P. The compound does not react with sodium and with PCl_5 under ordinary condition.

Calculate the empirical and molecular formula of the compound. Name one possible compound and write its structure.

(b) Mention one method for preparing the compound. $7+3=10$

10; Mention one chemical reaction in each case for distinguishing between the following pairs of organic compounds :

(a) Ethylene and acetylene.
(b) Acetyl chloride and acetic anhydride.
(c) Benzene and toluene.
(d) Acetaldehyde and acetone.
(e) Acetamide and acetonitrile. $2\times5=10$

11. (a) How are the following functional groups introduced in the benzene ring :

(i) $-COOH$ (ii) $-NH_2$ (iii) $-OH$

(b) How is phenol separated from a mixture of benzene and phenol ? $6+4=10$

12. (a) Write structural formulae of the compounds $(A-D)$ in the following reactions :

$$\text{Calcium acetate} \xrightarrow{\text{Distillation}} A \xrightarrow[\text{Sodium acetate}]{\text{Semicarbazide hydrochloride} \atop +} B$$

(ii) $$\text{Ethyl alcohol} \xrightarrow[H_2SO_4]{K_2Cr_2O_7 \atop +} C \xrightarrow[\text{NaOH Solution}]{\text{Cold dilute}} D$$

(b) State the steps mentioning the reagents in the following transformations :

(i) Formic acid from acetic acid.
(ii) Ethyl alcohol from acetylene.

(c) Explain what is meant by 'Metamerism'. 4+4+2=10

CHEMISTRY—1985

First Paper

Group—A

(Answer Question 1 and any *three* from the rest)

1. (a) A compound containing two nitrogen atoms in its molecule has 30-48% of nitrogen. Calculate the molecular weight of the compound. (N=14)

(b) How many atoms will be present in 0·05 mole of ozone ? 4+1

Or, (a) A gaseous hydrocarbon requires six times its own volume of oxygen gas for complete oxidation and produces four times its own volume of carbon dioxide gas. What is its formula ?

(b) Vapour density of a compound of empirical formula CH_2O is 90. What is the molecular formula of the compound ? (C=12, H=1, O=16) 4+1

2. Ammonia contains 82·35% nitrogen, water contains 11·11% hydrogen and nitrogen peroxide contains 69·57% oxygen. Show that the above results can be explained with the helf of a law chemical combination. State this law. Explain the law with the help of Dalton's atomic theory. 5+2+3

3. (a) State Le Chatelier's Principle.

Describe the effects of changes of pressure and temperature on the position of equilibrium of the following gaseous reaction :

$$H_2+I_2 \rightleftharpoons 2HI—13 \text{ kcal.}$$

(b) Volume of a given mass of a gas at fixed pressure changes from 1 litre to 1·3 litre due to a change of temperature from 0°C to 82°C. Determine the value of absolute zero (in centigrade scale) on the basis of above results. 6+4

4. (a) State Dulong and Petit's law. How it this law applied to find out the atomic weight of an element ? What are the limitations of the method ?

(b) 1·08 gm of a metal produces. 1·435 gm. of chloride. Specific heat of the metal is ·059. What Is its actual atomic weight ? (Cl=35·5) 6+4

5. (a) Calcium carbonate is precipitated when Sodium carbonate solution is added to Calcium chloride sulution. Similar precipitation of Ferric carbonate does not occur when Sodium canbonate solution is added to Ferrie chloride solution. Why is it so ?

(b) What is an indicator ? Which indicators would you use for the following neutralisation reactions :

(i) Hydrochloric acid by sodium carbonate.

(ii) Oxalic acid by Sodium hydroxide.

(c) In what proportion by volume should a 0·5 N acid solution be mixed with a 0.3 N alkali solution to get a 0.05 N alkali solution. 3+3+4

6. (a) What is oxidation number ? How will you differentiate it from vatency ?

(b) Balance the following equation by oxidation number method :

$$H_2S+SO_2 \rightarrow S+H_2O$$

(c) Zinc replaces silver from siver nitrate solution but silver cannot replace zinc from zinc nitrate solution. Explain why. 5+3+2

Group—B

(Answer Question 7 and three from the rest)

7. (a) Give one reaction to show that Hydrogen can act as an oxidising agent.

(b) Why pure zinc cannot be used for the preparation of hydrogen from dilute Sulphuric acid ?

(c) What is nascent hydrogen ? 2+2+1

Or, (a) What concentrated Sulphuric acid is not used for the preparation of Hydrogen peroxide from Barium peroxide ?

(b) Concentrated Hydrochloric acid is not used for the preparation of nitric acid from potassium nitrate.

(c) What is laughing gas ? 2+2+1

8. (a) Describe the preparation of dry Sulphur dioxide gas in the laboratory.

(b) State (with chemical equations) the reaction of chlorine gas with the following reagents :

(i) Hot and conc. Caustic soda solution and

(ii) Aqueous solution of Sulphur dioxide. $6+2\times2$

9. What is a chemical fertiliser ? Describe briefly the technical methods for the preparation of (a) a fertiliser containing nitrogen (b) a fertiliser containing calcium. $2+4\times2$

10. A Sodium Salt (A) on heating gives a substance (B) and oxygen gas. B gives brown fumes (C) on being heated with dilute acid. When B is heated with Ammonium chloride, a colourles gas (D) and a solid residue (E) is obtatined. A, on being heated with Ammonium chloride gives another colourless gas (F) and the solid residue (E). Identify A, B, C, D, E and F and write down the chemical reactions with equations. $3+7$

11. State with chemical equations, what happens when (any five) :

(a) Water is added drop by drop into a mixture of red phosphorous and iodine.

(b) Hydrogen Sulphide gas is passed into a solution containing cupric chloride and zinc chloride acidified wite dilute hydrochloric acid.

(c) Hydrogen peroxide is added to a solution of potassium dichromate acidified with dilute Sulphuric acid.

(d) Sulphur is boiled with concentrated nitric acid.

(e) Powdered charcoal if heated with concentrated nitric acid.

(f) Ammonia solution is added gradually to a solution of silver nitrate.

(g) Sodium nitric solution is heated with aluminium powder and caustic soda. 2×5

12. Explain why (any five)

(a) Coal gas may be poisonous.

(b) While diluting Sulphuric acid, acid is added slowly to water.

(c) Sulphur dioxide has no bleaching action in absence of moisture.

(d) Nitrogen obtained from air is slightly heavier than nitrogen obtained from Ammonium nitrite.

(e) Carbon dioxide is a gas, while Silicon dioxide is a solid.

(f) Diamond is very hard while graphite is soft.

(g) Hydrogen iodide cannot be dried by concentrated sulphuric acid. 2×5

CHEMISTRY—1985

2nd Paper

Group A

Answer any to quessions

1. (a) Arrange the following elements in the order of increasing electronegativity :

Cl, Mg, C, S

(b) How many protons are present in 5·6 litres at N. T. P. of oxygen gas containing O^{16} isotopes only.

(c) Calculate the numbers of alpha and beta particles emitted for the following radio-active change :

$${}_{90}X^{232} \rightarrow {}_{82}Z^{208}$$

(d) State the nature of bonds in the following compound :

MgO, Cl_2O, Ca_3N_2, HBr.

(e) Define isotope with one example. 2×5

2. (a) Three elements A, B and C have atomic numbers $z-2$, z and $z+1$ respectively. Of the three, B is an inert gas.

(i) Which one has the highest value of electronegativity ?

(ii) Which one has the highest ionisation potential ?

(iii) What is the formula of the compound formed between A and C ?

(iv) What will be the nature of the bond between A and C in the compound formed ?

(b) State the differences of the properties of the electrovalent and covalent compounds. Why are the ionic compounds said to contain no real bond ?

(c) State which of the following compounds are polar and which are non-polar :

SO_2, CO_2, N_2O, H_2O 4+4+2

3. (a) Account for the following :

(i) Boiling point of ethyl alcohol is higher than that of dimethyl either though they have the same molecular formula.

(ii) Magnesium hydroxide is soluble in ammonium Chloride solution.

(iii) An ion is more stable than the atom from which it is derived.

(b) 0·499 gm of a crystalline salt gives out 0·18 gm of water vapour on being heated to produce the anhydrous salt. If the molecular weight of the crystalline salt be 249·5 find out the no of molecules of water of crystallisation present in a molecule of the crystalline salt. $2 \times 3 + 4$

4. (a) Explain the basic difference between the phenomena of the flow of electricity through a metallic wire and that through an electrolyte.

(b) Why sodium is not liberated at the cathode when an aqueous solution of sodium chloride is electrolysed ?

(c) Explain what happens when copper sulphate solution is subjected to electrolysis using platinum electrodes.

(d) A solution of a salt of a metal of atomic weight 112 was electrolysed for 15 minutes with a current of 1·5 amperes. If the increase in weight of the cathode be $0{\cdot}78\bar{8}$ gm., find the valency of the metal in this salt. $2+2+2+4$

Group—B

Answer any two Questions

5. (a) In connection with the extraction of Aluminium from Bauxite, furnish the following information :

(i) Composition of the electrolyte.

(ii) Nature of electrodes and electrode reactions.

(iii) Collection of the metal.

(b) Name a metal which can be extracted by the self-reduction process. Give equations of all the chemical reactions that occur during the extraction of the metal from its ore. $5+5$

6. (a) Arrange the following compounds is the order of increasing basicity :

$$MgO, ZnO, CaO, Na_2O$$

(b) Name the metals having the following ores :

(i) Chalcopyrite ; (ii) Magnetite.

(c) Name the constituents of the following alloys :

(i) Bronze ; (ii) Stainless Steel.

(d) What is zinc amalgam ? How is it prepared ?

(e) Compare Galvanization with tin plating. 2×5

7. (a) Outline the method of preparation and use of any two of the following :

(i) Cuprous Chloride.

(ii) Anhydrous aluminium chloride

(iii) Bleaching powder.

(b) State with equations that happens when (attempt any two.)

(i) Sodium nitrate solution is warmed with zinc dust and caustic soda solution.

(ii) Potassium iodide solution is added to copper sulphate solution.

(iii) Carbon dioxide gas is passed into brine saturated with ammonia gas. 6+4

Group C

(Answer any three questions)

8. (a) Account for the following :

(i) The valency of carbon is four although its electronic configuration $1s^2\ 2s^2\ 2p^2$.

(i) Ethyl alcohol and formic acid have identical molecular weight, but the boiling point of the former is about 22°C lower than that of the latter.

(b) Two different monohydric alcohols A and B have the same composition :

$C=60\%$, $H=13{\cdot}3\%$, $O=26{\cdot}7\%$. When passed over hot alumina in the vapour state, both form the same compound C which decolorises dil. $KMnO_4$ solution.

What are the structures of A, B and C ? Name them according to the I. U. P. A. C. system of nomenclature.

What happens when vapours of A and B are separately passed over hot copper oxide ? 3+7

9. (a) Name the reagents necessary for the following transformations :

(i) Acetone→Diactone alcohol.

(ii) Ethyl alcohol→Chloroform.

(iii) Benzene diazonium chloride→Chloro benzene,

(iv) Acetic anhydride→Ethyl acetate.

(b) State one chemical reaction in each case by which you can distinguish between the following pairs of organic compounds :

(i) Formic acid and acetic acid.

(ii) Methyl alcohol and ethyl alcohol.

(iii) Methyl amine and acetamide. 4+6

10. (a) How are the following functional groups introduced into the benzene ring ?

(i) $-NH_2$, (ii) $-COOH$, (iii) $-I$

(b) How is pure aniline prepared from nitrobenzene ? 6+4

11. (a) Identify A—F in the following reactions :

(i) $C_6H_6 \xrightarrow[\text{Anhydrous } AlCl_3]{CH_3COCl} A \xrightarrow[HCl]{Zn/Hg} B$

(ii) $C_2H_2 \xrightarrow[80°C]{Hg^{+2},\ 20\%H_2SO_4} C \xrightarrow{K_2Cr_2O_7 + H_2SO_4} D$

(iii) $C_6H_5NO_2 \xrightarrow{Sn + HCl} E \xrightarrow{NaNO_2 + HCl} F$

(b) Write short notes on :

(i) Friedel-craft's reaction.

(ii) Cannizaro's reaction. 6+4

12. (a) Explain the use of the following substances in organic chemistry with examples :

(i) Anhydrous $AlCl_3$

(ii) $LiAlH_4$

(iii) Sodalime.

(b) What is Markownikoff's rule ? Explain with an example. Under what conditions is the rule violated ? 6+4

CHEMISTRY—1986

First Paper

Group A

Answer any Four questions.

1. The percentages of oxygen in two oxides of a metal are 22·22 and 30 respectively. Show that the above result follows a law of chemical combination. State the concerned law. If the formula of the second oxide be M_2O_3, find that of the first. 6+2+2=10

2. (a) State Avogadro's hypothesis and establish the reationship between molecular weight and vapour density of a gas with is help.

(b) 1·2 gm of a gas occupies 1000 millilitre at 27°C and 700 mm. pressure of mercury. The gas is an element and its molecules are diatomic. What is the weight of one atom of this gas ?

2+4+4=10

3. (a) What do you understand by the equivalent weight of an element ? Prove that the atomic weight of an element is equal to or simple multiple of its equivalent weight.

(b) 20·55 ml. of dry hydrogen gas at standard temperature and pressure are produced by the action of 0·06 gm of a metal with dilute sulphuric acid. The solution obtained as a result of this reaction gives on evaporation and subsequent cooling a crystalline substance which is isomorphous with $FeSO_4$, $7H_2O$. Determine the equivalent weight and exact atomic weight of the metal.

5+5=10

4. (a) State Dalton's Law of partial pressure.

(b) A compound contains 10·04% carbon. 0·84% Hydrogen and 89·12% Chlorine. Determine the empirical formula of the compound.

(c) 1 gm of pure $CaCO_3$ is dissolved completely in 40 ml. of a Hydrochloric acid solution. The resultant solution requires 40 ml of 0·5 N NaOH solution for complete neutralisation. Find out the strength of Hydrochloric acid solution.

(d) Which indicator would you use during the neutralisation of Acetic acid by sodium hydroxide ? 2+3+4+1=10

5. (a) Find the value of molar gas constant R in litreatmosphere after stating the units of P, V and T.

(b) Explain with reasons why an aqueous solution of NH_4Cl reacts acidic.

(c) Show reasons why Magnesium can liberate Hydrogen from an aqueous solution of Hydrochloric acid while copper cannot liberate Hydrogen.

(d) 10 ml. of a gaseous Hydrocarbon were exploded with 25 ml. of Oxygen and cooled. The gas mixture occupied a volume of 15 ml. On treatment with KOH there was a further contraction of 10 ml. Find the molecular formula of the Hydrocarbon.

2+2+2+4=10

6. (a) Express the equilibrium constant of the reaction :

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_2(g)$$

in the forms K_p and K_C and find out the relation between these two constants.

(b) Determine the oxidation number of Mn in K_2MnO_4.

(c) Balance by oxidation number method :

$$FeCl_2—H_2S=FeCl_2+S+HCl.$$

(d) "Concentration of Sodium Chloride Solution is expressed in formality but not in molarity."— Give reasons. 3+2+3+2=10

Group B

Answer any *Four* questions

7. Mixture of a white solid A and a black solid B gives on heating a white solid K and a gas D, while B remains unchanged. If A alone is heated C and D are obtained but it requires higher temperature and the reaction proceeds slowly. When aqueous solution of Silver Nitrate is added to an aqueous solution of C, a white precipitate of E is obtained. E is completely soluble in excess of ammonia solution. The gas D when mixed with Nitric Oxide gas forms another red colured gas F.

(i) Identify A, B, C, D, E and F. Write down the *names* only.

(ii) For each chemical reaction give equations only.

(iii) What is the function of B while producing C and D from A ?

(iv) Name another substance which will perform the same function as B. 3+5+1+1=10

8. (a) Describe the method of preparation of chlorine gas in rhe laboratory.

(b) With the help of a chemical reaction show that Iodine acts as an oxidising agent.

(c) How can a small quantity of chlorine mixed with oxygen gas be removed ? 6+2+2=10

9. Explain the following statements with reasons :—

(a) Carbon dioxide gas cannot extinguish fire caused by burning magnesium metal.

(b) If one touches white phosphorus, one's hands are to be washed with copper sulphate solution.

(c) Sulphur dioxide have both oxidising and reducing properties.

(d) Hydrogen bromide cannot be prepared by the action of concentrated sulphuric acid on sodium bromide.

(e) Ozone gas is prepared by silent electric discharge through oxygen. 2 × 5 = 10

10. State what happens when with equations (any *five*) :—

(a) Potassium Nitrite solution is added to Potassium iodide solution acidified with dilute sulphuric acid.

(b) Phosphine gas is passed into acidified copper sulphate solution.

(c) Sodium Formate is heated with concentrated sulphuric acid.

(d) Concentrated Sulphuric acid is added to a mixture of solutions of Ferrous Sulphate and Potassium Nitrate.

(e) Aqueous solution of hydrogen peroxide is added to alkaline Potassium ferricyanide solution.

(f) Ozone gas is passed through stannous chloride solution containing hydrochloric acid. 2 × 5 = 10

11. How will you show that (any *five*) :—

(a) Nascent Hydrogen is more powerful reducing agent than ordinary Hydrogen.

(b) Sulphur dioxide contains sulphur.

(c) Nitric acid contains hydrogen.

(d) Air is a mechanical mixture but not a chemical compound.

(e) Silicon dioxide is an acidic oxide.

(f) Phosphine has basic properties. 2 × 5 = 10

12. (a) How Sulphuric acid is manufactured by contact process ?

(b) Describe with equations how Urea is manufactured from Ammonia.

(c) State what happens when Orthophosphoric acid is heated slowly to a high temperature. Give equations. 5 + 3 + 2 = 10

CHEMISTRY—1986

Second Paper

Group A

Answer any two questions.

1. What are alpha, beta and gamma rays? Compare the following properties of them :—

(a) Velocity.

(b) Penetrating power and

(c) Kinetic energy.

Why Rutherford's atomic model had to be rejected? What are the chief characteristics of Bohr's atomic model?

$2+3+2+3=10$

2. (a) What informations are obtained from solubility curve? [Mention any two informations.]

1000 ml. of a saturated solution of KNO_3 of sp. gr. 1·332 at 25°C was completely evaporated to dryness. The dry residue weighed 333 gm. Calculate the solubility of KNO_3 at 25°C.

Name one solid substance whose solubility decreases with increase of temperature.

(b) Explain why AgCl is more soluble in pure water than in dilute hydrochloric acid solution.

(c) Which of the two molecules $CHCl_3$ and CCl_4 is polar and why?

$5+3+2=10$

3. (a) What is understood by electronegativity of an element? How does it change in a period?

(b) Define coordinate bond. Give one example.

(e) What are the defects of the periodic table?

(d) The electron arrangement of an element is.

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2.$$

To which period and group does this element belong in the Periodic Table? What is this element? What is valency?

$2+3+3+2=10$

4. (a) State Faraday's two laws of electrolysis. Deduce an expression combining these two laws.

(b Compare thermal dissociation with electrolytic dissociation.

(c) How many electrons pass through the solution to the anode when 1·00 gm of Copper is deposited by passing current through $CuSO_4$ sulution ?

[Cu = 63·5, F = 96500 coulomb]. 5+2+3=10

Group B

Answer any *two* questions.

5. (a) How pure Alumina is obtained from Bauxite ore ?

(b) Describe briefly the principle of extraction of metal by carbon reduction process.

(c) State briefly the chemical reactions, that occur in the blast furnace during extraction of Iron. 4+2+4=10

6. (a) How are the following substances prepared ?

Mention one use of each one of them. (answer any *three*) :—

(i) Bleaching Powder

(ii) Plaster of Paris

(iii) Blue Vitriol

(iv) Sodium Bicarbonate.

(b) What is galvanisation ? 3 × 3 + 1 = 10

7. (a) State with equations that happens when (any three) :

(i) Dry ammonia gas is passed over metallic sodium at about 400°C and the product is treated with water.

(ii) Excess caustic soda solution is slowly added to a solution of Aluminium Sulphate solution.

(iii) Excess Potassium Cyanide solution is gradually added to Copper Sulphate solulion.

(iv) SO_2 gas is passed first slowly and then in excess through freshly prepared lime water.

(b) Arrange the following substances in order of the increasing Carbon content in them :—

Cast Iron, Wrought Iron and Steel. 3 × 3 + 1 = 10

Group C

Answer question No. 8 and *Two* from the rest.

8. An organic compound A has the molecular formula C_8H_6O. It reacts with phenyl hydrozine to give phenyl hydrazine and also forms iodofoim when reacted upon by iodine and alkali. On reduction A forms an alcohol (B). The vapour of B when passed over heated alumina forms an olefin (C). C on ozonolysis gives acetaldehyde and formaldehyde. Write down the structures and names of A, B and C. Justify your answer with reasons. 10

Or,

(i) Assume that ethyl alcohol is dehydrated to ethylene in the laboratory in 50% yield and that the ethylene so obtained combines with bromine in 80% yield. Calculate the weight of ethylene-dibromide that can be obtained from 0·5 mole of ethanol. (Atomic wt. of Bromine = 80).

(ii) Identify an aliphatic liquid compound which is soluble in water, liberates CO_2 from Na_2CO_3 and reduces both $KMnO_4$ solution and Tollen's reagent. Give reasons for your answer with equations. 5+5=10

9. (a) State with eqations what happens when (any *five*) :—

(i) An aqueous solution of Sodium Acetate is electrolysed in between two Platinum electrodes.

(ii) Ethylene dibromide is boiled wlth alcoholic KOH Solution.

(iii) Formaldehyde is treated with concentrated ammonia solution.

(iv) Acetamide is treated with Sodium Nitrite and dil Hydrochloric acid solution.

(v) Aniline is treated with excess Bromine water.

(vi) Benzene is boiled for several hours with conc. H_2SO_4

(b) How acetic acid is prepared commercially ? $2 \times 5 + 5 = 15$

10. (a) Describe the laboratory method of preparation of acetylene. How this gas is purified ?

(b) State one chemical reaction in each case by which you can distinguish between the following pairs of organic compounds (any *five*) :

(i) Formic acid and Acetic acid.

(ii) Methyl amine and Aniline.

(iii) Acetyl chloride and Acetic Anhydride.

(iv) Diethyl ether and Ethyl alcohol.

(v) Acetaldehyde and Acetone.

(vi) Ethyl Alcohol and Phenol. 5+2×5=15

11. (a) How pure aniline is prepared in the laboratory ?

(b) Starting from aniline how can you prepare the following compounds ?

(i) Toluene

(ii) Nitrobenzene

(iii) Benzoic Acid.

(iv) Phenol.

State the steps mentioning the necessary reagents and conditions in each case. 7+4×2=15

12. (a) Identify the organic products (A—G) in the following reactions :—

(i) $CH_2—CH=CH_2 \xrightarrow{HBr} A \xrightarrow{KCN} B \xrightarrow[\text{Heat}]{H^{\mp},\ H_2O} C$

(ii) $C_6H_5OH \xrightarrow[\text{Distillation}]{\text{Zn dust}} D \xrightarrow[60°C]{\text{conc } HNO_3 \,|\, \text{conc } H_2SO_4} E \xrightarrow{Sn/HCl} F \xrightarrow[\text{Heat}]{CHCl_3+KOH} G.$

(b) Write short notes on any *two* of the following :—

(i) Chlorination of Toluene

(ii) Wurtz reaction

(iii) Haloform reaction. 7+2×4=15

1987

CHEMISTRY

FIRST PAPER

Group A

Answer any Four *questions*

1. 1 gramme of a metal having no variable valency produces 1·67 gramme of oxide when heated in air. Its carbonate contains 28·57 percent of the metal. How much oxide will be obtained by heating 1 gramme of the carbonate? Which law of chemical combination has been used in the above calculation? State the law. Cite one example to show that the opposite statement of the law is not always true.

2. (*a*) State Avogadro's hypothesis. Show with its help that the gramme molecular volume of any gas at N.T.P. is 22·4 litres.

(*b*) Under the same conditions of temperature and pressure 1 litre of a gaseous element (Molecular formula X_2) reacts with 2 litres of another gaseous element (Molecular formula Y_2) to form 1 litre of a gaseous compound. What will be the molecular formula of the compound?

3. (*a*) What is gaseous diffusion? State Graham's law of gaseous diffusion. Cite one example of its practical application.

(*b*) 432 ml. of a gas *A* takes 36 minutes to pass out through a fine hole. 288 ml. of another gas *B* takes 48 minutes to come out through the same hole under the same conditions of temperature and pressure. If the molecular weight of *B* be 64, what is the molecular weight of *A*?

4. (*a*) What do you mean by the terms efflorescence and deliquescence? Give one example in each case. Explain why crystals of some salts behave as such.

(*b*) *Explain with reasons :—*

(i) Liquid Hydrogen chloride does not conduct electricity while electricity flows easily through an aqueous solution of HCI.

(ii) When electricity is passed through a dilute aqueous solution of H_2SO_4 using two Platinum electrodes Hydrogen and Oxygen are obtained ? But during electrolysis of cold concentrated H_2SO_4 (50%) using Platinum electrodes and high current density Hydrogen and Perdisulphuric acid are produced.

5. (*a*) Chemical reaction that takes place during the manufacture of ammonia by Haber's process is as follows :

$$N_2 \text{ (gas)} + 3\,H_2 \text{ (gas)} \rightleftharpoons 2\,NH_3 \text{ (gas)} + 11{\cdot}8 \text{ KCal.}$$

State the necessary principle and explain the effects of changes of temperature and pressure on this reaction with the help of that principle.

(*b*) 2·925 gm of pure NaCl is dissolved in a volumetric flask and volume of the solution is made upto 250 c.c. 25 c.c. of this solution required 40 c.c. of a $AgNO_3$ solution to precipitate all the chloride as AgCl. Determine the strength of this $AgNO_3$ solution. [Na=23, Cl=35·5]

6. (*a*) State Dulong and Petit's law. Explain how this law helps in the determination of atomic weight.

(*b*) When electricity is passed through an acidified $CuSO_4$ solution in between two Platinum electrodes 6·35 gm of copper is liberated at the cathode :

(i) How many coulomb of electricity is required for this purpose ?

(ii) How many atoms of copper are liberated at the cathode ?

(iii) What change will be observed during this electrolysis if copper electrodes are used instead of Platinum Electrodes :

You must have to show reasons in support of your answer in each case. [Cu = 63.5]

Group B

Answer any Four *questions*

7. State the difficulties encountered during the preparation of fluorine gas. How fluorine gas is prepared by removing these difficulties ? Show with the help of a chemical reaction that the reactivity slowly decreases from Fluorine to Iodine.

8. Explain the following statements with reasons :—

(*a*) Most of the metals do not give hydrogen by reaction with nitric acid.

(*b*) Aqueous solution of borax is alkaline.

(*c*) Blue flames are seen over 'chulas' using coal as fuel.

(*d*) Hard water is unsuitable for use in boilers.

(*e*) When PH_3 gas is prepared in the laboratory, the air inside the flask is replaced by coal gas ?

9. State what happens when with equations :—

(*a*) Sulphur dioxide gas is passed into a suspension of Iodine in water.

(*b*) Bromine is added dropwise to a mixture of red phosphorous and water.

(*c*) Carbon dioxide gas is passed into a suspension of Barium peroxide in water.

(*d*) Ammonia gas is passed through an aqueous solution of Ferric chloride.

(*e*) Aqueous solution of Hydrogen sulphide gas is added to an aqueous solution of Hydrogen peroxide.

10. (*a*) Write down the names of principal constituents of coal gas.

(*b*) What by-products are obtained during the manufacture of coal gas ?

(*c*) Describe the manufacturing process of Nitric acid from Ammonia. Give necessary equations. [Figure not required]

11. (*a*) State one chemical reaction in each case to distinguish between the following pairs of compounds :—

(i) Sodium Nitrate and Sodium Nitrite.
(ii) Carbondioxide and Sulphurdioxide.
(iii) Sodium Sulphate and Sodium Sulphite.
(iv) Water and Hydrogen peroxide.

(*b*) How oxygen is obtained from Lead Nitrate ?

12. (*a*) Six chemical reactions are taking place in the following six steps :—

(1) A white solid *A* gives on heating another white solid *B*, a colourless and nearly odourless gas *C* and water vapour. (2) *B* gives the gas *C* on reaction with dil. Hydrochloric acid. (3) when *C* is passed through conc. caustic soda solution, it first produces *B* and (4) on passing excess *C* through the solution *B* is converted into *A*. (5) when aq. solution of calcium chloride is added to an aq. solution of *B* a white precipitate *D* is obtained. (6) *D* is completely soluble in dilute Hydrochloric acid yielding the gas *C*.

(i) Identify by *A*, *B*, *C* and *D*. Write down names only.
(ii) Represent the different chemical reactions occurring in steps 1 to 6 by means of chemical equations only, mentioning the corresponding number of the step.

(*b*) State two uses of this gas *C*.

1988

CHEMISTRY

First Paper

Answer any *four* questions.

Group—A

1. (a) State the law of reciprocal proportion. Give one example.

(b) Analysis of any of the gaseous compounds of phosphorous shows that 1 litre of it at N.T.P. never contains less than 1·384 gm of this element. Again one litre of phosphorous vapour at N.T.P. weighs 5·536 gm. What conclusions can be drawn regarding approximate atomic weight of phosphorous, its molecular weight and atomicity of phosphorous from above results.

(c) Distinguish between the atomic weight and the weight of one atom of the element.

2. (a) State Dalton's law of partial pressure.

(b) A mixture containing 1·0 gram hydrogen and 4·0 gram oxygen is kept at 27°C in a vessel whose volume is 20·0 litres. Calculate the total pressure of the mixture and partial pressures of hydrogen and oxygen in the vessel.

(c) State Charle's Law. Find the value of molar gas constant R in calories per degree kelvin per mole.

3. (a) 1 gm. of pure anhydrous Na_2CO_3 is dissolved in water inside a 1000 ml. volumetric flask and volume made upto the mark with water.

Give reasons whether this solution is a standard solution or not.

(b) Why hydrochloric acid is called a strong acid while acetic acid a weak one ?

(c) To 50 ml. solution containing a mixture of NaOH and Na_2CO_3 are added a few drops of phenolphthalein and on addition of 60 ml. (N) HCl the pink colour just disappears. The same colourless solution is again titrated with the same acid after addition of methyl orange and 20 ml. of the acid just turns it faint pink.

Calculate the strength of NaOH and Na_2CO_3 in the mixture in terms of gms per litre of the solution.

4. (a) State Law of Mass action.•What is "active mass" ?

(b) The following chemical reaction

N_2 (gas)$+3H_2$ (gas)$\rightleftharpoons$ $2NH_3$ (gas)+22000 cal. is at equilibrium at 550°C and 200 :atmospheric pressure. In which direction the equilibrium will be shifted if :—

(i) Some quantity of hydrogen gas is introduced in the system from outside at the same pressure and temperature.

(ii) Ammonia gas formed is absorbed in water. How can these results be explained by Le Chateliar's principle ?

(c) Deduce a relation between the equilibrium constant Kp and Kc for the reaction.

$2\ SO_2$ (gas)$+O_2$ (gas)$\rightleftharpoons$$2\ SO_3$ (gas)+45 K cal at a temperature 450°C

(d) Why :there will be difference in the results if $CaCO_3$ is heated in the open and in the closed vessel ?

5. (a) What is water of crystallisation ?

(b) 0.2 gram of Magnesium is completely dissolved in dilute H_2SO_4 solution. The volume of dry hydrogen gas collected was found to be 185 ml at N.T.P. Calculate the equivalent of Magnesium.

(c) What is a Colloidal solution ? How does it differ from a true solution ?

(d) With the help of Faraday's laws of electrolysis, calculate the charge of an electron.

6. (a) 60 ml of a mixture of CO and H_2 was mixed with 40 ml oxygen and exploded in an eudiometer. After cooling, the volume was found to be 30 ml. Find the composition of the original mixture (All volumes were measured at the same pressure and temperature).

(b) Explain with one example what is meant by an amphoteric oxide.

(c) Why an aqueous solution of NH_4Cl is acidic ?

(d) Define :—Supersaturated solution.

(1987 and 1988) New Syllabus

Group—B

Answer any *four* questions

7. Six chemical reactions are taking place in the following six steps.

(1) pungent smelling colourless gas A (highly soluble in water) reacts with another pungent smelling gas B (which is colourless and also highly soluble in water) to produce a white solid C. (2) A when passed over heated Na at high temperature produce a solid compound D and H_2 gas. (3) An aq. solution of A when added to aq. $ZnSO_4$ solution a white precipitate E is obtained. (4) The white precipitate E dissolves in excess aq. solution of A to form a soluble compound F. (5) Aq. solution of B when added to aq. $AgNo_3$ solution, a white precipitate G comes out. (6) When iron powder is added to an aq. solution of B, a soluble compound H is formed and hydrogen gas is evolved.

(i) Identify A, B, C, D, E, F, G and H. Write down names only.

(ii) Represent different chemical reactions occuring in steps 1 to 6 by means of chemical equations only, mentioning the correct number of the step.

8. State what happens when with equations :—

(a) H_2S gas is passed over a filter paper soaked in Lead Acetate Solution and the paper is subsiquently dipped in an aq. solution of hydrogen peroxide.

(b) Potassium cyanide solution is slowly added in excess to copper sulphate solution.

(c) Ozone is mixed with sulpher dioxide gas.

(d) Solid Iodine is added to a solution of Potassium Iodide.

9. (a) What are the evidences in favour of the fact that air is a mechanical mixture ?

(b) How hydrogen gas can be obtained from Nitric acid ?

(c) How borax is prepared from Colemenite ?

10. (a) Describe the laboratory method of preparation of chlorine gas.

(b) Show by equations that sulphur dioxide acts both as an oxidising agent as well as a reducing agent.

(c) Show how chlorine acts as a bleaching agent.

11. Explain why :—

(a) F_2 cannot be prepared by electrolysis of aqueous HF solution.

(b) P_2O_5 is not used for drying ammonia gas.

(c) Hydrogen bromide cannot be prepared by the action of concentrated sulphuric acid on sodium bromide.

(d) Silent electric discharge is passed in the preparation of ozone from oxygen.

(e) In the laboratory method of preparation of PH_3, the air inside the flask (in which PH_3 is prepared) is replaced by coal gas.

12. (a) Describe the manufacture of H_2SO_4 by contact process.

(b) What are the by products (Any four) in the manufacture of coal gas ?

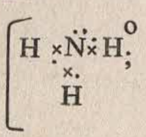
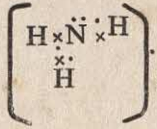
(c) What is fertiliser ? Name two nitrogenous fertiliser.

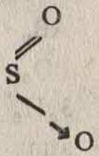
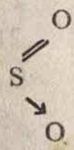
ERRATA

PART I

Page	Line	For	Read
23	17	relats	relates
38	25	Ferreous	Ferrous
44	21	AB_y	A_xB_y
82	last line	PO_5	P_2O_5
93	5	3_2H_2	$\frac{3}{2}H_2$
107	last line	atm)	1 (atm)
170	1 of the exercise	KnO_3	KNO_3
242	Equ (12·6)	$\frac{E}{E_H}=\frac{Z}{E_H}$	$\frac{F}{E_H}=\frac{Z}{Z_H}$
		$=\text{Or } \frac{E}{E_H}\times Z_H$	$=\text{Or } Z=\frac{E}{E_H}\times Z_H$
250	2	(vol)	(volt)
250	18	$A^{-}\!-A+xe$	$A\overset{-x}{\rightarrow}A+xe$

PART II

Page	Line	For	Read
1	12	Is	Is^1
5	17	sction	action
11	17	Propertris	Properties
26	31	alcoho	alcohol
33	21	$50^{-}_{2}, 2P_2O'_5$	$50_2, 2P_2O_5$
36	last line	he	the
43	12	 $\left[H\ {}^{\times}_{\vdots}\underset{\overset{\times\cdot}{H}}{\overset{\cdot\cdot}{N}}{\times}H^{o}_{;}\right.$ electron from N × electron from H	 $\left[H\,{}^{\times}_{\vdots}\underset{\overset{\times\cdot}{\ddot{H}}}{\overset{\cdot\cdot}{N}}\,{}^{\cdot}_{\times}H\right)$. electron from N. × ; electron from H
45	last line	^{o}	$\overset{o}{H}_2$

60	2	acctic	acetic
135	Fig 24·4	sodium	Potassium
141	Fig 24·10	HNO_2	HNO_3
154	8	Propertiss	Properties
190	22	whiie	white
214	Fig 29·4	S--S	S—S
215	Fig	S--S	S—S
230	12		

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This book has been written primarily to meet the requirement of students at the Higher Secondary level and conforms to the revised syllabus of the West Bengal Council of Higher Secondary education. This is a learning-oriented text book, neither too elementary nor too exhaustive for the plus-two standard. The subject matter has been written in simple and lucid language supplemented with worked out problems, so that students can grasp the fundamentals and upgrade their standard. In this respect, the book has its own merit and excellence in comparison with other books. The book should be of value to all budding scientists who really take interest in the subject.

B.C. Sen, M.Sc., D.Phil, is an experienced and distinguished professor of Chemistry in the West Bengal Senior Educational Service. He has a long teaching experience of more than thirty years in various government colleges. He used to teach Physical Chemistry to both undergraduate and postgraduate classes. Dr. Sen is now the professor of Chemistry, Presidency College, Calcutta. His special fields of interest are statistical mechanics, molecular thermodynamics, irreversible thermodynamics, chemical kinetics, soil chemistry and allied topics.